Electronic structure of clean and carbon-covered closed-packed rhodium and ruthenium surfaces

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In order to determine the nature of the active species which several groups have found to be important in catalytic carbon hydrogenation reactions, self-consistent linear combination of atomic orbitals (LCAO) calculations have been performed of the electronic structure of clean and C-covered Rh(111) and Ru(0001) surfaces. Apart from the shift of the Fermi level to higher energy to accomodate an extra electron per atom in Rh, the results are quite similar for the two metals. A (1×1) layer of C's, occupying threefold-coordination sites binds by forming tetrahedral bonds with its neighbors, leaving a nonbonding p_z band at the Fermi energy. Thus the model C species examined here should be very reactive. Additionally, the $C 2s - C 2p_z$ binding-energy difference is about 10 eV, in accord with the Auger-peak separation seen by Goodman et al. for a reactive carbidic layer on Ni. Partial local density of states (LDOS) and energy-band dispersion curves are presented to permit the verification of the model carbidic overlayer. Results presented for the clean surfaces include work functions that are in excellent accord with the measured values, and band dispersions, notably a surface resonance band that has been observed on Ru, by Himpsel et al. Finally, surface-bulk core-level binding-energy shifts have been calculated. For the clean surfaces, they are in reasonable agreement with empirical heats of segregation. For the C-covered surfaces, they indicate that C binds most strongly to Ru, followed by Rh and Pd.

I. INTRODUCTION

One of the principal goals of surface science is to demonstrate its own utility in the analysis of "real-world" catalysis. An important experimental step in this direction has been the recent use, by several groups,[1-3] of double-purpose surface-analysis systems. These consist of two chambers. In one, chemical reactions can be carried out at relatively high pressures and temperatures on very clean substrates with extremely pure reactants. In the other, the connecting chamber system, the surface on which the chemistry happens can be studied with the usual battery of spectroscopic tools, e.g., Auger, low-energy electron diffraction (LEED), high-resolution low-energy electron-loss spectroscopy, etc.

A particularly thorough study of a catalytic reaction that made use of such a surface-analysis system was recently reported by Goodman et al.,[1] who studied CO methanation over a Ni(100) single-crystal surface. Perhaps the most important result of this work was the demonstration that the "turnover number," i.e., the CH_4 production rate normalized to the number of exposed Ni atoms is virtually identical, for the single crystal, to its values for a finely dispersed, Al_2O_3-supported, real-world catalyst. The activation energy for the reaction is also essentially the same on the single-crystal and powdered-Ni catalysts. Thus the correspondence seen by Goodman et al. between methanation rates and spectroscopically characterizable forms of carbon on the Ni surface is of profound interest. If we can interpret the observed spectra terms of a geometric model, then we can identify a chemically active species that plays an important role in an actual catalytic reaction.

In fact, two distinct surface carbon species were identified in Ref. 1, as shown in Fig. 1. A carbon adlayer whose carbon Auger spectrum appears to be very similar to that of carbon in graphite was produced when the methanation reaction was run at too high a temperature. This "graphitic" overlayer was found to be chemically inactive when the sample was returned to the reaction chamber. On the other hand, a "carbidic" overlayer, that is, one whose carbon Auger line resembles that of C in bulk nickel carbide, was found to be catalytically active. For example, if after measuring its Auger spectrum a substrate was returned to the reaction chamber, upon admission of H_2 gas the initial methane-production rate was found to be propor-
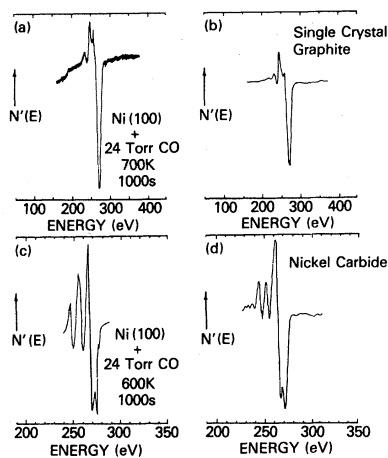
FIG. 1. Reproduced from Ref. 1, Auger spectra of (a) inactive C species on Ni(100), (b) single-crystal graphite, (c) active C species on Ni(100), and (d) C in nickel carbide. The reason for labeling the active and inactive species carbidic and graphitic is clear.

tional to the peak-to-peak height of the just measured carbidic Auger line. These results pose several obvious questions: What is the nature of the carbidic overlayer? Why is it chemically active? In what way does the carbidic species differ from the graphitic that explains the relative inactivity of the latter?

Although the most detailed study of hydrogenation reaction over single-crystal catalysts has been performed for Ni (several different faces have been looked at by now), similar conclusions have beeen drawn in studies carried out on Ru, Fe, and Rh surfaces.[2−4] This is significant from the theorist's viewpoint, not only in that the activity of carbidic-surface carbon species appears to be general, but also because Ni is not the ideal material for a theoretical interpretation of electronic structure versus surface geometry. Because it has a narrow band of holes near the Fermi energy, it is not possible to achieve a correspondence between calculated band-structure and angle-resolved photoemission data in the usual way.[5] Correlation effects must be explicitly considered.[6,7] Additionally, Ni is magnetic, which means that below the Curie temperature the matrices involved in an electronic structure calculation must be $2N \times 2N$, where as for a similar nonmagnetic material they would be $N \times N$. Both of these facts imply that the use of electronic structure calculations to identify the geometry of an overlayer on Ni by comparing them to electron

spectroscopic data and to interpret its chemical activity is less likely to succeed than it would be for a simpler catalyst material.

For these reasons, in an earlier attempt to understand chemically active carbidic-surface carbon, I calculated the properties of carbon overlayers on Ru(0001) (Ref. 8). This, however, was an unfortunate choice from an experimental point of view. The $3d$ core levels of Ru lie at 286 and 290 eV, while the $1s$ level of C is bound by 288 eV. As a consequence, it is difficult to use standard electron spectroscopic techniques [Auger or x-ray photoelectron spectroscopy (XPS)] to determine just how much carbon resides on an Ru surface, and therefore in the present paper, I report new results for C on Rh(111). Rh is also a good methanation catalyst. It is nonmagnetic, and its calculated band structure is in reasonable agreement with photoemission data. Its $3d$ electron binding energies are 313 and 318 eV, so that its $M_{4,5}VV$ Auger line does not interfere with the carbon Auger signal. (Also its $4p$ levels lie at 53 and 58 eV, so that there is no overlap between carbon KVV and the Rh $M_{4,5}N_{2,3}V$ lines.) Finally, although it is now doubted that CO dissociates on Rh(111) at lower pressure,[9] it is not unreasonable to expect that one can produce a carbidic overlayer on it similar to that which has been found to be important for Ni.[10]

The main results reported below show theoretically that the Ru and Rh close-packed surfaces should behave similarly. Their electronic structures are related by a "rigid-band" picture in which the most significant change in going from Ru to Rh is that the Fermi level moves higher to accommodate the one extra electron per metal atom. This is found to be the case both for the clean and the carbidic-carbon-covered surfaces. For both metals, the carbon forms tetrahedral s-p bonds with its three neighboring substrate atoms, leaving a nonbonding, dangling p_z band partially filled. In addition, a few eV above the Fermi energy there is a high density of states of p_x-p_y orbitals that are antibonding between the C atoms and the surface. These results show that the C species modeled should be very reactive. (As I showed in my earlier work for C on Ru,[8] the inactivity of graphitic C is due to the π bonding between the p_z orbitals. This occurs for graphitic C because neighboring C atoms are close enough for their p_z orbitals to overlap.)

All the results reported here are based on self-consistent linear combination of atomic orbitals (LCAO) calculations. The only physical approximation is the use of a local potential to describe the

effects of exchange and correlation. The main numerical approximation is the use of a basis of (atom-centered as well as "floating") s-like Gaussian functions to which the electron charge and potential are fitted. The method has been described in detail in an earlier publication.[11] Typically it yields very stable (converged) results for the electron spectrum relative to the Fermi energy. Because it is never easy to find a good Gaussian basis with which to fit the charge density as it becomes tenuous in the vacuum, the work function is generally determined less reliably.

In addition to results for C adsorption on Rh and Ru, I also report below a variety of results for the clean Rh(111) and Ru(0001) surfaces, including work functions, which agree unexpectedly well with experiment, local densities of state, surface-state dispersions, and surface core-level binding-energy shifts. The latter agree rather well with empirical values of segregation energies for Rh dissolved in Ru and Pd dissolved in Rh. This agreement encourages us to take the calculated values of the changes in surface core-level shifts due to carbon adsorption as measures of the corresponding, adsorption-modified segregation energies.

II. CLEAN Rh(111) AND Ru(0001)

To begin let us consider the clean close-packed surfaces of Rh and Ru for which LEED and photoemission data are available. According to the detailed LEED analysis of Shepherd et al.,[12] the clean Rh(111) surface is unreconstructed, and to within experimental error simply embodies an ideal termination of the bulk fcc crystal. The clean Ru(0001) surface is (1×1), but to date there has been no analysis of LEED intensity versus voltage data for it, so in what follows I have assumed it to be ideal as well. For both surfaces, I have found charge-potential bases that appear to be adequate far enough into the vacuum that the valence charge density has fallen to roughly $\frac{1}{30}$ to $\frac{1}{40}$ of the bulk average value. (Beyond this value, Gibbs oscillations[11] in the fit to the charge density become evident.) That this is an adequate basis for the charge may be judged from the agreement to within 0.1 eV of the calculated and measured values of the work functions. For Rh(111) and Ru(0001), I find work functions of 5.1 and 5.4 eV, respectively. A photoelectric value of 5.1 eV may be deduced from the photoemission data of Braun et al.[13] for Rh(111) and similarly, a value of 5.4 eV was obtained in the

ultraviolet photoelectron spectroscopy (UPS) experiment on Ru(0001) of Himpsel et al.[14] Calculated local densities of states for the close-packed Ru and Rh surfaces are shown in Fig. 2. In both cases one notes that, as usual, the LDOS's for the outermost atomic layers are narrower and shifted to smaller
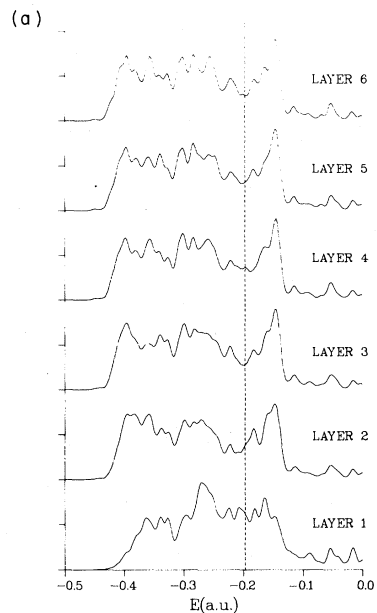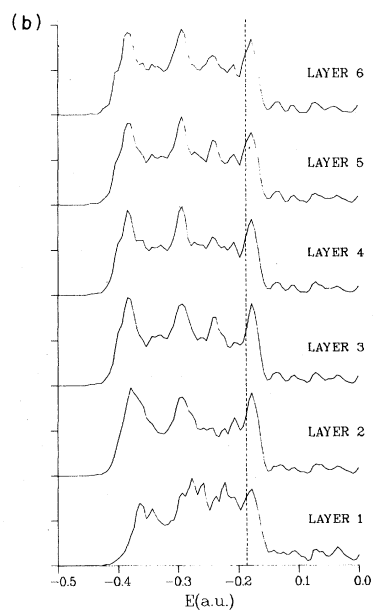

FIG. 2. Layerwise local densities of states for (a) 11-layer Ru(0001) and (b) Rh(111) slabs. Energies are in hartrees, relative to the vacuum level. Dotted lines indicate the Fermi energies. Layer 1 is the surface layer.

binding energies due to coordination with fewer neighbors. Since the hcp and fcc lattices differ only in their layer stacking, it is not surprising to note that the Ru and Rh LDOS's are similar in shape, and that the main difference between them is that the Fermi level lies higher in the Rh to accommodate the extra electron per atom in that metal.

Electron energy-level dispersions for 11-layer Ru(0001) and Rh(111) films are shown in Fig. 3. The levels that have large amplitude on outer layer atoms are indicated by heavy lines. Note that the projected bulk band structures as well as the positions of the surface-localized levels are again quite similar. [In this regard, one should bear in mind that although the hcp and fcc bulk Bravais lattices are different, the fcc(111) and hcp(0001) surfaces have the same rotation symmetry.] Throughout the central region of the surface Brillouin zone for both metals, the calculations predict a band of surface-localized states weakly split off the top of the s
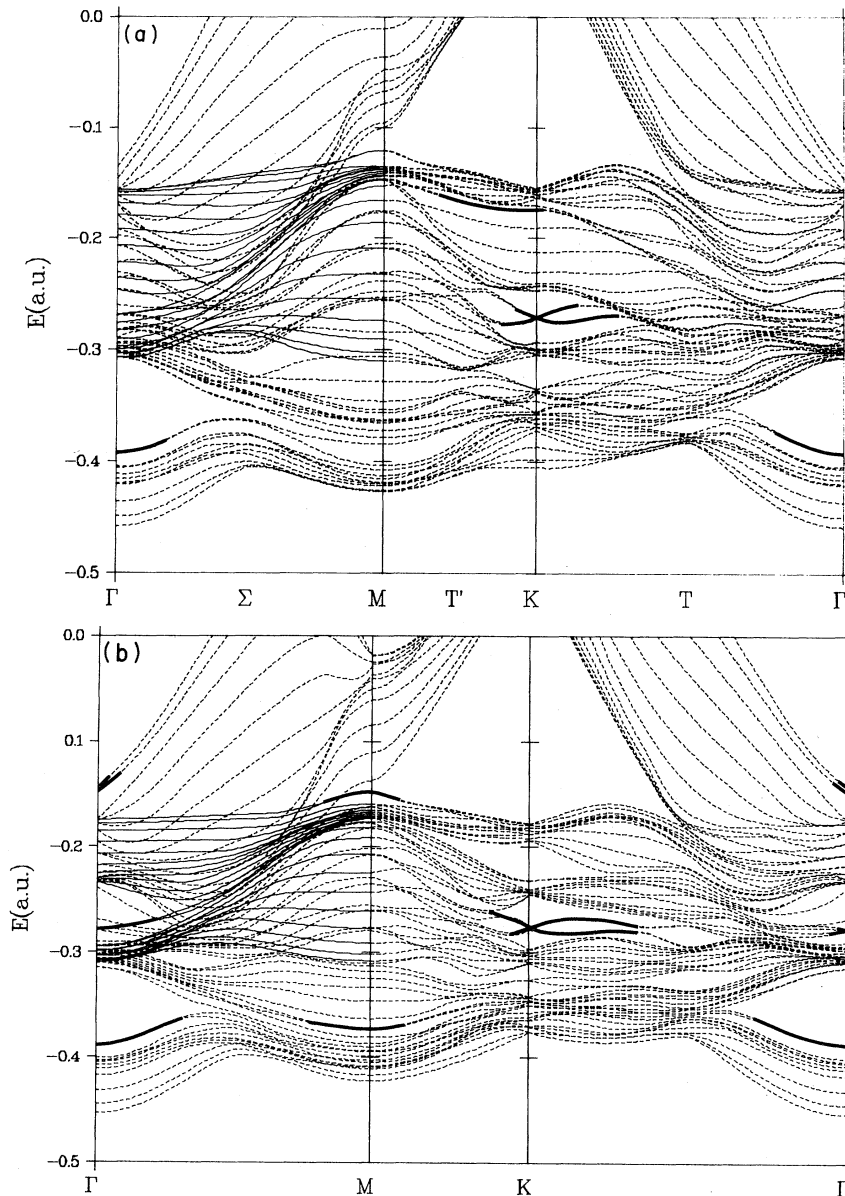

FIG. 3. Energy-level dispersions for (a) clean, 11-layer Ru(0001) and (b) Rh(111) films. Along the Γ-M symmetry line, states which are even with respect to the reflection plane are indicated with dashed lines while the odd states correspond to solid lines. States indicated with heavy lines are heavily weighted on the outer layer of the film.

band. This band starts at Γ from a binding energy of 5.3 eV relative to the Fermi energy for Ru (5.4 eV for Rh). A similar theoretical result has recently been reported for Ru by Holzwarth and Chelikowski,[15] while the UPS data of Himpsel et al.[14] indicate a rather broad surface state at Γ bound by 5.6 eV. No similar surface-state peak was reported in the UPS measurements on Rh(111) or Borstel et al.[13] However, this experiment was not carried out at a synchrotron, where photon energies above 41 eV would have been available. At somewhat higher energies one would expect the cross section of the state to be larger because of its significant 5s character. It is true that the surface-band position is sensitive to the spacing between the first and second Rh layers. A 10% expansion of this spacing, for example moves the state at the zone center 0.3 eV further out into the s-d hybridization gap. However, in view of the excellent agreement between the calculated and measured work functions for Rh(111) and the similarity of the calculated surface bands for Rh and Ru, one anticipates that a surface band similar to that observed for Ru will ultimately also be found for Rh.

III. SURFACE CORE-LEVEL BINDING-ENERGY SHIFTS: CLEAN Ru(0001) AND Rh(111)

In addition to valence-electron energy-level dispersions, core-level binding energies have been calculated for each layer of the Ru and Rh films due to the redistribution of charge associated with bonding. For the narrow 4f levels of several metals of the 5d series, the differences between surface- and bulk-atom core-level binding energies have been measured directly, but as yet no theoretical results have been published which would permit a comparison. For lighter metals, the core levels are sufficiently broad that the extraction of a credible value for the surface core-level binding-energy shift becomes a major, though not impossible undertaking.[16]

Generally, one expects that because of band narrowing at a surface, and because charge neutrality is preserved layerwise, surface core-level shifts will be increasingly negative toward the left-hand side of the Periodic Table, and increasingly positive toward the right-hand side.[17] Thus for Ti(0001) the surface-atom core levels are more strongly bound than in bulk, by 0.22 eV, while for Sc(0001) the corresponding shift is calculated to equal 0.48 eV. The results computed for Ru and Rh conform to this

picture. For Ru(0001) the surface core levels are shifted 0.5 eV to lesser binding energy, while for Rh(111) the calculated shift is 0.6 eV.

Despite the fact that, because the core levels are too broad, there has been no attempt to measure the surface core-level shifts for Ru and Rh, it is possible to assess our results in comparison to reality, though by a rather circuitous route. Rosengren and Johansson[18] (RJ) have recently pointed out that the surface core-level shift[19] in metal Z is equal to the heat of surface segregation of solute atoms of charge $Z + 1$. The argument is based on the equivalent-atom picture, that says that as far as the valence bands are concerned there is no difference between an atom of charge Z that has a core hole and an atom of charge $Z + 1$ in the same location. RJ's argument does require one to assume that the core-level binding energy is the energy necessary to remove an electron and leave a fully screened core hole behind. However, to the extent that the energies involved in screening surface and bulk core holes do not differ, this complication can be ignored, and the surface core-level one-electron energy shift (the "chemical shift") can be compared to the appropriate heat of segregation.

The only problem is where does one find a value for the heat of segregation for the Rh atoms to the surface of a dilute alloy of Rh in Ru, or for Pd in Rh? Here we make use of the empirical studies of Miedema[20] whose formulas for heats of segregation have proven reasonably accurate in the cases where they have been tested. According to Miedema, the heat of segregation of element A which is in dilute solution in host metal B is given by

$$H_{\text{seg}} = \tfrac{1}{3}[0.7H_{\text{soln}} - c(\gamma_A - \gamma_B)V_A^{2/3}] . \quad (1)$$

Here H_{soln} is the heat of solution of A in B, the γ's are the surface energies of liquid metals A and B, c is a universal constant, and V_A is a parameter representing the volume of atom A. Miedema's corrections involving differing atomic volumes have here been ignored because Ru, Rh, and Pd are roughly comparable in metallic radius. Without worrying about the microscopic underpinnings of Eq. (1), it can be used to obtain an estimate of the heats of segregation of Rh to the surface of Ru(0001) and of Pd to the surface of Rh(111) for comparison with the calculated core-level binding-energy shifts.

I have taken values of the γ's for this comparison from Miedema's tables, and for the necessary heats of solution, I have used values of the cohesive energies of pure metallic Ru, Rh, and Pd and of the in-

termetallic compounds Ru_3Rh and Rh_3Pd (Cu_3Au structure) computed by Moruzzi, Gelatt, and Williams.[21] These calculations give heats of solution of 0.05 eV for Rh in Ru and 0.45 eV for Pd in Rh. (Thus at zero temperature neither Rh would dissolve in Ru nor Pd in Rh.) Miedema's empirical formula[22] yields values of these heats of solution equal to 0.05 and 0.08 eV.

The results of the calculation are that the heat of segregation of Rh to an Ru surface is 0.2 eV, while for Pd to an Rh surface, depending on whether I use the former or latter value of the heat of solution, it is 0.5 or 0.4 eV. Considering the crudeness of these estimates, which, for example, make no mention of which crystal face is involved, the rough agreement in magnitude and trend of the heats of segregation and core-level energy shifts is gratifying. Incidentally, it should be noted that in the estimates of the heats of segregation the largest contribution is that of the surface-energy difference, not the heat of solution. Thus the driving force for segregation is that Pd has a lower surface energy than Rh, whose surface energy is in turn lower than that of Ru.

I return to the subject of core-level binding-energy shifts in Sec. V below, for a discussion of the effect of C adsorption on their values.

IV. CARBON OVERLAYERS

In choosing a model for carbidic carbon on Ru or Rh, the selection is currently severely limited by the requirement of computational feasibility.[23] Specifically, in order to keep the required matrices sufficiently small while retaining a metal film of adequate thickness that the two surfaces can be assumed to be independent, I am unable to consider overlayers that are of lower symmetry than that of the clean surface. Thus, I have restricted consideration to (1×1) overlayers with the C atoms lying on any of the three symmetry axes normal to the close-packed, clean surface. Fortunately, as discussed earlier,[8] this restriction does not prevent one from considering graphitic as well as carbidic models. The distance between the inequivalent three-fold sites on Ru(0001) and similarly on Rh(111), is only about 10% longer than the C—C bond length in graphite. So filling both these sites with C atoms is a reasonable model for a graphitic overlayer. Filling only one of the three-fold coordinated sites, on the other hand, makes the C-C distance equal to the metal-metal nearest-neighbor distance (5.01 a.u. for Ru and 5.09 a.u. for Rh, compared to a C-C distance of 2.68 a.u. in graphite). This is sufficiently large that the π bonding which is responsible for the inactivity of graphitic C can no longer occur. So although hydrogenation reactions are strongly suppressed when the C coverage is too high, presumably because there is not enough room for the H molecules to dissociate, stick to and move about the surface, the (1×1) C overlayer model should give a reasonable picture of the electronic structure of relatively "isolated" carbon species. (Incidentally, Fig. 1 shows "electronically" that the carbidic-C overlayer is comprised of C's that are much more isolated than in graphite. That is, the structure of the carbidic Auger line is relatively sharp, which is expected if the C-C interaction is relatively weak.)

Figure 4 compares the LDOS's for carbidic overlayers on the Ru and Rh surfaces. In the case of Ru the carbon atoms occupy hcp three-fold coordination sites (that is, sites with a second-layer Ru atom directly below) at a distance of 2.41 a.u. above the outer Ru layer. The Ru—C bond length in this configuration is 3.81 a.u. (2.01 Å). The curves for Rh correspond to C's in the fcc sites (no second-layer Rh directly below). Here the C adlayer is 2.72 a.u. above the outer Rh layer, and the Rh—C bond length is 4.00 a.u. (2.12 Å). (This value is chosen to equal the sum of the Rh and C covalent radii.)

One notices many similarities in Fig. 4. In both cases, it is evident that the bonding between the C atoms and the surface is the result of the formation of bonding combinations of the $C 2s$, $C 2p_{x,y}$, and the metal orbitals. On the other hand, the $C 2p_z$ orbitals are nonbonding. In the C atom the p_x, p_y, and p_z states are obviously degenerate. But in Fig. 4, one sees that the p_x and p_y density is pulled down several volts, while the p_z DOS remains at the Fermi energy. These results indicate that on both metals, the C atoms bond to the surface by forming three tetrahedral bonds to the neighboring metal atoms, leaving a dangling p_z orbital unsaturated. Evidently in this situation, the C atoms are very reactive, eager to lower the energy of the z orbital by forming a C—H bond, for example.

Besides the nonbonding z orbitals, one notes in Fig. 4 a large density of unfilled $C 2p_x$ — and $C 2p_y$ —metal antibonding states. Filling these levels by bonding with more than one H atom would lower their energy, and at the same time weaken the C—metal bond.

In the case of Ru, I have evaluated the electronic structure of the carbidic overlayer at two other values of the separation between the C and outer-

LDOS's Ru(0001)-C(1x1), 3-fold site

(a)

Ru, Layer 2

C p_z

C p_x, p_y

C s

Ru, Layer 1

E(a.u.)
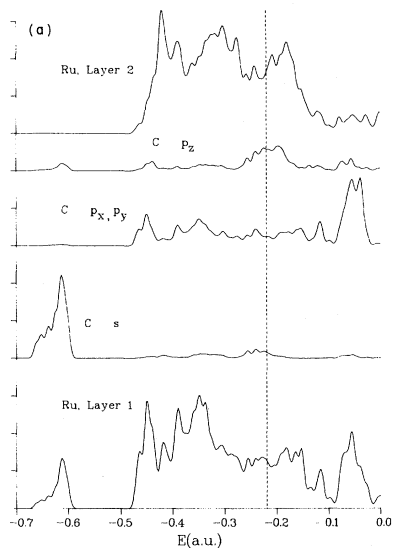
LDOS's Rh(111)-C(1x1), fcc site

(b)

Rh, Layer 2

C p_z

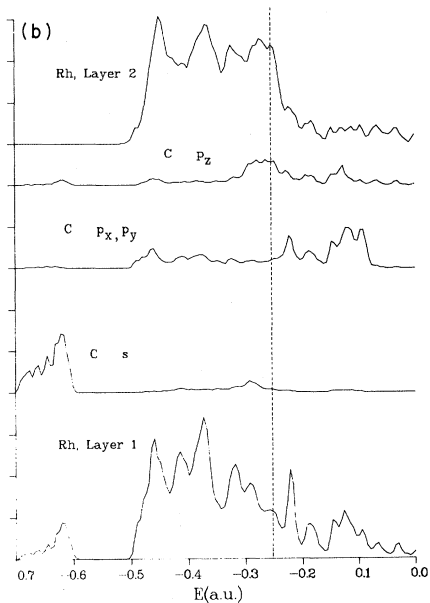C p_x, p_y

C s

Rh, Layer 1

E(a.u.)

FIG. 4. Partial, layerwise local densities of states for (a) 11-layer Ru(0001) and (b) Rh(111) films with carbidic overlayers on each surface. (See text for the defintion of carbidic.)

most Ru layers. A number of interesting results of these calculations are indicated in Table I. Focus first on the location of the peak in the C 2s—derived DOS relative to the Fermi energy. As one would expect for a bonding level, as the C-Ru distance decreases, its binding energy increases

in magnitude. Now let us compare to the data for C on Ni, on the assumption that the results for Ru and Ni will not be terribly different. In Goodman's Auger data for carbidic C on Ni, there are three prominent features superimposed on a squarish background.[24] On the basis of the LDOS curves shown in Fig. 4, it would seem reasonable to identify the three features with Auger decays involving, respectively, two Cp_z electrons, one Cp_z and one C2s electron, and two C2s's.[25] Since the Cp_x, p_y LDOS is broad, overlapping the entire Ru d band, Auger emission involving these electrons contributes mainly to the broad component of the Auger line. With this identification of the features in the carbidic Auger line shape, the separation of the features must equal the position of the C2s level relative to the Fermi energy (where the p_z level lies). In the data of Goodman et al., the peak separation is about 10 eV or 0.368 a.u. This value is in reasonable agreement with the C2s binding energy found for the most likely separation of our C layer from Ru. Moreover, since the binding energy of this bonding level depends sensitively on C—metal bond length, the Auger measurement may be used to help determine this length. Incidentally, note that for the one calculated C-Rh distance, the C2s—derived peak lines 0.382 a.u. = 10.4 eV below the Fermi level, again in rough agreement with the result of Goodman et al. for C on Ni.

In all the calculations I have done, the C overlayer results in a work-function increase. For C on Ru at the separation of 2.41 a.u. between the C and outermost Ru layers for which (Table I) the valence electron energy is lowest, the predicted work-function increase is 0.60 eV. To date, the only carbidic overlayers that have been looked at involved much lower than monolayer coverage, and it is not known whether the low coverage involved island formation or not. Thus, even if there had been a change of work-function measurement, it is not clear that it should be compared to the number just quoted. At this stage one must therefore be content to note that the value $+ 0.6$ eV is not an unreasonable one, and distinguishes the carbidic phase from the graphitic, for which the work-function change has the opposite sign. (Indeed, the predicted and observed work function for a graphite overlayer is virtually that of native graphite, 4.1 eV.[26])

A more detailed picture of the results of Fig. 4 can be seen in the surface-band structures shown for C on Ru and C on Rh in Fig. 5. The similarity of the results, i.e., the validity of a rigid-band picture, is striking. One notes ample opportunities for ex-

TABLE I. Results for various spacings of the model carbidic layer on Ru and Rh surfaces, including the work function Φ, the depth of the C$2s$ peak below the Fermi energy, and for the Ru cases, the total valence electron energy of a five-layer metal film with a carbidic layer on either side.

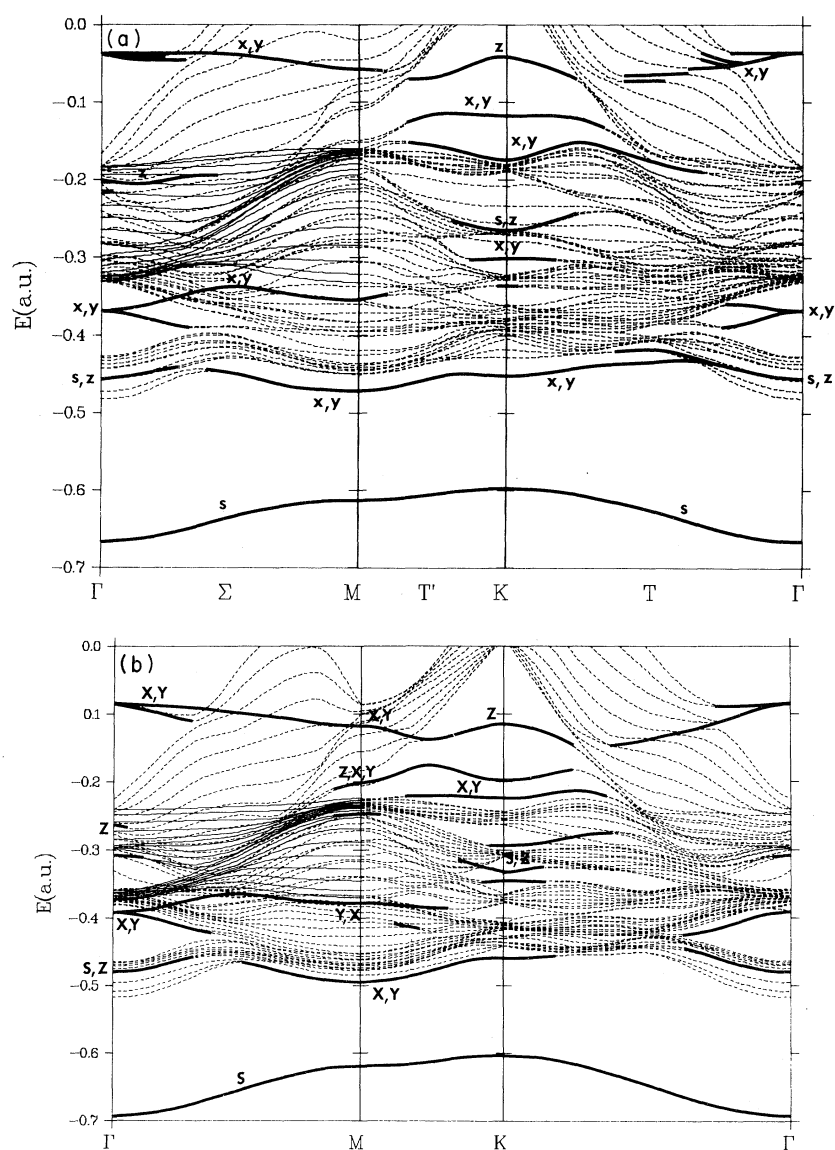| System	C-Metal Layer spacing (a.u.)	Φ (eV)	C$2s$ peak (eV)	E_{tot} (a.u.)
C on Ru(0001)	1.91	5.5	11.8	−97.037
C on Ru(0001)	2.41	6.0	10.0	−97.059
C on Ru(0001)	2.91	6.3	9.7	−94.014
C on Rh(111)	2.72	6.8	10.4	

FIG. 5. Energy-level dispersions for (a) 11-layer Ru(0001) and (b) Rh(111) film covered by carbidic overlayers. Along the Γ-M symmetry line, states which are even with respect to the reflection plane are indicated with dashed lines while the odd states correspond to solid lines. States indicated with heavy lines are heavily weighted on the outer layers of the film. Main angular momentum components of the states that have heavy weight on the C atoms are noted.

perimental tests of the model of carbidic presented here [provided that a (1×1) overlayer can be realized if only in islands]. Besides the $C\,2s-$ and $C\,2p_x, p_y-$ derived bands which occupy virtually the entire surface Brillouin zone, and should be visible in angle-resolved UPS, the antibonding p_x, p_y bands should be prominent in electron energy-loss or inverse-photoemission experiments. To date there has been only one attempt to characterize a carbidic overlayer by other than Auger spectroscopy.[26] However, the conclusion was that in the UPS experiment, only a graphitic overlayer was ever produced. An important message of that failure is that in order to carry out surface analyses of chemically interesting substrates, it would be extraordinarily useful to build on to one's ultrahigh vacuum (UHV) system, a chamber in which chemistry can be carried out at high pressures, under highly controlled conditions.

V. CORE-LEVEL SHIFTS AND SEGREGATION WITH A CARBIDIC OVERLAYER

A final piece of information concerning the electronic structure of carbidic overlayers of Ru(0001) and Rh(111) is the effect of the C layer on the core-level binding-energy shift between surface and bulk metal atoms. Since the arguments of Rosengren and Johansson are independent of whether there is an overlayer or not, these binding energies tell us whether and the extent to which a carbidic layer draws Rh atoms to the surface of Ru or Pd atoms to the surface of Rh.

In fact the effect is just the opposite. For the carbidic layer adsorbed at the most probable separation on Ru, the binding energy of a core electron in the outermost Ru layer is 0.31 eV greater than that for a bulk Ru atom. Similarly for the carbidic layer on Rh, the core levels on the outermost Rh's are 0.15 eV deeper than on the bulk Rh atoms. Thus the adsorption of the C layer for both metals reverses the sign of the heat of surface segregation for the atom of charge $Z+1$. The physical interpretation of this effect is obvious, in terms of Eq. (1). Adsorption can have no effect on the heat of solution. Thus the effect on the heat of segregation must involve the relative surface energies of the solute and solvent

species, in the presence of the carbidic adlayer. If the solute element is the more strongly bound to the carbon, then the system can reduce its energy by segregating it to the outer layer, and conversely, if the solvent binds more strongly to the C layer. Our calculated results here show that while clean Ru, Rh, and Pd have successively smaller surface energies, adding a carbidic overlayer reverses the order to Pd, Rh, and Ru.

VI. FUTURE DIRECTIONS

From the experimental point of view, what is needed now is a more detailed characterization of carbidic carbon. The desirability is clear of building onto vibrational loss spectroscopy, photoemission, and surface extended x-ray absorption fine-structure apparatuses, antechambers that permit the preparation of chemically interesting characterizable surfaces. From the theoretical side, the most important problem is to make it less demanding of computer resources to study surface systems of lower symmetry. Although it is not unlikely that the (1×1) carbidic-overlayer model discussed here represents a lower-coverage state reasonably well, it is hard to see how similar methods will ever be used to trace the rest of the pathway leading, for example, to methanation. For the present, only cluster methods are available to handle such problems. But in general the comparison of cluster results to experiments on well-characterized surface systems is problematic. What would really be desirable is a convenient way of solving the surface impurity problem analogous to methods that have recently proven successful in the study of defects in bulk solids. Work on this problem is in progress.[27]

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[19] In stating this result one must be careful about signs. Specifically, the correct statement is that the energy required to exchange a bulk, $Z + 1$ impurity atom with one in the surface layer equals the ionization potential (a positive number) of a core level in a surface layer atom of charge Z minus the ionization potential of the same core level in a bulk atom of charge Z. If we then define the core-level energy shift as the energy relative to the vacuum of the core level in a surface atom (a negative number) minus that for a bulk atom, we see that if surface core levels lie deeper than bulk ones, so that the surface core-level shift is negative, then it costs energy to put an impurity atom at the surface and heat of segregation is negative.

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[23] The use of a LAPW code instead of the Gaussian LCAO program used here may mitigate this problem somewhat.

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[25] In making this identification, it is assumed that the Auger line shape represents a self-convolution of the C LDOS. This has been shown to be a reasonable assumption for C in bulk TiC (D. R. Jennison, unpublished), and should generally be the case for non-closed-shell systems, because of effective initial-state screening [see P. J. Feibelman, J. Vac. Sci. Technol. 17, 176 (1980)].

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