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Copper on Ni(111): The electron states from submonolayer to several-monolayer coverages

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Experimental and theoretical results are presented for Cu on an Ni(111) surface. Angle-integrated ultraviolet photoelectron spectroscopy (UPS) results ($h\nu = 21.2$ eV) are given for Ni(111) with increasing Cu coverages θ from 0.1 to 4 monolayers. The results at $\theta \ll 1$ refer to isolated Cu adatoms and those at $1 < \theta < 4$ to an ordered overlayer. The position and line shape of the Cu 3d peak are the same for $0.1 < \theta < 1$: This indicates that the main features of the Cu 3d band are determined by the interaction of Cu atoms with the substrate atoms. Evidence for such interaction is provided by the modifications of the substrate photoemission, which take place upon Cu deposition. At $\theta \simeq 4$ the line shape is more similar to that of bulk Cu. These results appear to be typical of the interaction of Cu atoms with a d-metal substrate: Comparison with those of a Cu monolayer deposited on an sp metal [Cu on Zn(0001)] shows that the Cu 3d peak is found at higher binding energy with respect to the Fermi energy. The monolayer case is discussed in detail in connection with theoretical results of a tight-binding calculation. The local density of states (LDS) calculated for the Cu overlayer, the Ni underlayers, and for the clean Ni(111) surface shows clearly the importance of the d-d interaction between Cu and Ni atoms. The theory accounts for the Cu 3d-peak position and the modification of the substrate density of states. Also, the measured Cu 3d line shape can be understood on the basis of the theory. The experimental and theoretical results are also discussed in connection with other available information on related topics.

I. INTRODUCTION

A great experimental[1-6] and theoretical effort[7-14, 5] has been recently devoted to the study of the electronic structure of very thin slabs (from one monolayer to a few layers) of noble and transition metals. This problem is important to elucidate the transition from isolated atoms to bulk materials and to understand some aspects of the surface physics of these metals (e.g., band narrowing). Since the experimental work is necessarily carried out on thin layers deposited onto a substrate, any effort to compare experiment with theory calls for experiments of well-characterized situations which can be compared with reliable calculations. This is the case of ordered overlayers on a crystalline substrate. We have previously made a theoretical and experimental study[5] for an ordered Cu monolayer on Zn(0001), and we have shown that the electronic structure of the overlayer is similar to that of a Cu(111) unsupported monolayer and that the Cu 3d band is narrower and shifted to higher binding energies with respect to bulk Cu. The 3d band narrowing is found in Cu crystal surfaces also[15] and is a well-established feature common to all calculated densities of states for surfaces and monolayers.[5, 7, 11-17] The shift to higher binding energies has been found experimentally in Ref. 5 as well as in measurements for Cu deposited on carbon.[6] It is theoretically more controversial, since it has not been found in other calculations which give a d band closer to the Fermi energy than in the bulk.[11-14]

In order to discuss the experimental results it is important to clarify better the role of the interaction with the substrate and to perform calculations closely parallel to the experiments. We have thus carried out an investigation of Cu deposited on Ni(111), where the interaction of the copper d states with those of the substrate is expected to be as strong as in Cu-Ni alloys. In a sense this case is opposite to that of Cu on Zn, which behaves basically as a free-electron substrate, due to the great energy separation between Zn and Cu d bands. This is the first experimental and theoretical work on a Cu overlayer strongly interacting with a d-band substrate.

We were able to prepare an ordered monolayer of Cu on Ni(111), and we discuss in this paper the results from angle-integrated ultraviolet photoemission spectroscopy together with density-of-states calculations. We present experimental results for other coverages (from 0.1 to 4 monolayers) since they shed light on the interaction between Cu and the substrate.

The paper is organized as follows: After a description of the experimental method in Sec. II, we give in Sec. III the experimental data and in Sec. IV the theoretical results. Section V is devoted to the discussion of the results, while Sec. VI includes comparison with previous experimental and theoretical work and the conclusions.

II. EXPERIMENTAL METHODS AND TECHNIQUES

The angle-integrated photoelectron energy distribution curves (EDC's) were measured with a spherical grid retarding potential analyzer. HeI light ($h\nu = 21.2$ eV) was incident normally on the sample. The base pressure in the chamber was 10^{-10} Torr. The sample manipulator could be cooled to ≃80 K [hereafter called conventionally LNT (liquid-nitrogen temperature)] and heated up 600 °C. An Auger-LEED (low-energy electron diffraction) apparatus was also available in the vacuum chamber. The Ni(111) substrate ($\frac{1}{4}$-in. diameter) was spark cut from a single crystal and mechanically polished. The surface was cleaned *in situ*. We used argon sputtering at 400–500 °C to remove impurities (sulfur segregates at the surface at high temperature) followed by oxidation (10 min at 350°C in 4×10^{-7} Torr of oxygen) to remove the residual carbon. Finally the surface was reduced with hydrogen and annealed at 300 °C. The copper was evaporated thermally from a bead on a tungsten wire and the deposition rate was controlled by a quartz oscillator with an accuracy for the determination of the coverage of about ±10%. Auger spectra were taken at selected times to monitor the surface cleanliness. We have studied increasing Cu coverages from $\theta = 0.1$ to $\theta = 4$ (in monolayer units). After the measurements at one coverage the sample was cleaned again and a new deposition was made.

III. EXPERIMENTAL RESULTS

The study by LEED and photoemission of the growth mechanism of Cu on Ni(111) held at various temperatures is beyond the purpose of the present work and will be reported elsewhere.[18] We give here only the necessary information about the structure of the overlayer to give a clear indication of the surface condition during the experiment.

On the basis of the LEED pattern we can say what follows.

(i) For submonolayer coverages we have not found evidence of a superstructure indicating a periodic overlayer: The LEED pattern of the substrate is always seen, indicating that the atoms of copper continue the substrate structure, but are not arranged in a periodic way.

(ii) Around $\theta \simeq 1$ the samples prepared at room temperature (RT) or prepared at LNT and successively heated at RT show an excellent (111) pattern. Only a small increase in the background is noted. The situation is clearly analogous to that of the Ni(001) substrate,[19,20] where the Cu growth is known to be epitaxic but with some defects, which can originate the weak background.

(iii) For $\theta \simeq 4$ the overlayer shows a (111) orientation.

As we will show later no Cu agglomeration occurs on the surface so that the ultraviolet photoemission spectroscopy (UPS) measurements at $\theta > 1$ refer to a uniform and periodic overlayer.

We give in Fig. 1 the EDC's taken at RT from Ni(111) with increasing Cu coverages; for comparison we give also the EDC from the clean Ni(111) surface, in excellent agreement with the literature,[21] and from a thick Cu layer (200 Å) measured at RT with the same apparatus. The results are the average of several measurements on different sample preparations, each giving reproducible results. In the figure the prominent peak due to Cu 3*d* electrons is clearly located at −2.85 eV and shifts slightly to lower binding energies at higher coverages, although the centroid of the peak is not changed upon increasing deposition. The EDC's are the same for samples prepared at RT or prepared at LNT and successively heated to RT. The EDC's from samples prepared at LNT measured at LNT before any heating are very similar to those taken at RT: The Cu 3*d* peak position and the modification of the Ni photoemission are exactly the same, while the Cu peak is somewhat broader at LNT (12% around $\theta = 1$). Owing to this strong similarity they will not be reported here. The small broadening could be due to the fact that some Cu atoms are in nonequivalent sites. The electron-state information given by the present EDC's will be discussed later; we give here only some comments which are relevant to complement the structural information given above.

The attenuation of the photoemission near E_F with respect to pure Ni is caused by the Cu overlayer, which has a much smaller density of states and photoemission cross section. By considering this attenuation we can evaluate the escape depth of the photoelectrons through the overlayer. We have obtained about 8 Å for electrons having energy 20 eV above E_F by assuming a uniform overlayer. This value is in good agreement with the known escape depth of Cu (Ref. 22) and indicates that the assumption of a uniform overlayer is correct within experimental accuracy. If the overlayer were discontinuous, as in the case of a nonuniform deposition, the apparent escape depth estimated by this method would be larger. The

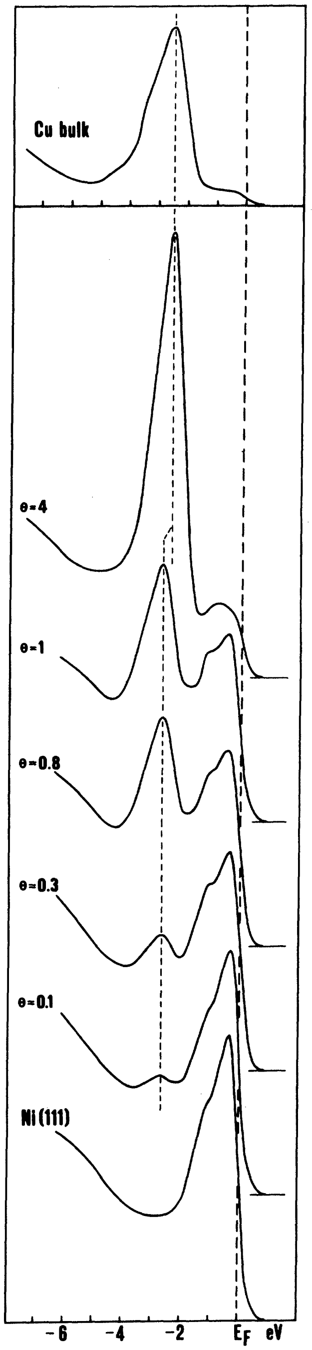

FIG. 1. Angle-integrated energy distribution curves ($h\nu = 21.2$ eV) from the clean Ni(111) crystal and from Ni(111) with increasing Cu coverages. The measurements were carried out on samples at RT after deposition at LNT. The coverage is expressed in monolayers. The upper EDC refers to bulk copper (in this EDC the ordinates are reduced by a factor of 0.25).

absence of agglomeration is consistent with what is known about surface diffusion. Self-diffusion data[23, 24] have been published for Ni(110). The surface diffusion of Cu on Ni should not be very different, since Cu and Ni are contiguous in the Periodic Table. The extrapolation to LNT of these data gives values which are nearly 30 orders of magnitude lower than those which could cause agglomeration on the time scale of the experiments, even in the less favorable case of diffusion along the 110 channels. It can be concluded that agglomeration is absent at LNT. On the other hand, the Cu 3*d* peak location is the same as at RT. This means that the measurements at RT for very low coverages refer to isolated atoms statistically distributed on the surface, so that the lateral interactions between adatoms can be neglected.

IV. THEORETICAL RESULTS

A theoretical investigation is of great help in the discussion of the previous results; this is possible if the calculations are sufficiently reliable to be compared with the experiments. This is the case of local density-of-states (LDS) calculations for ordered overlayers. Since at submonolayer coverages no ordered superstructure is obtained we have not tried to carry out calculations for these cases. We performed calculations for the monolayer case, which is the most significant among the situations where an ordered overlayer has been observed in the present experiments. In effect, the $\theta = 4$ case is less interesting, because it is closer to the bulk situation. We limited ourselves to the monolayer case also because the purpose of the calculation was to give a guideline to the discussion of the results rather than a complete theory of the experiment.

The Ni substrate is described by a slab of 13 (111) atomic planes with the sequence and spacing of the perfect crystal. Two (111) planes of Cu atoms with the same periodicity and the same planar lattice constant (≈2.6% less than in bulk Cu) of the substrate are present at the two sides of the slab in regular stacking sequence.

The method of calculation is outlined in Ref. 5. The one-electron crystal Hamiltonian of the slab is written in a basis of a nine two-dimensional Bloch sums of *sp*-*d* orbitals per atomic plane in the Slater-Koster scheme.[25] The values of the tight-binding parameters are from an accurate parametrization of the published bulk band structure of Cu (Ref. 26) and Ni (Ref. 27).

The exchange splitting and thus the ferromagnetic nature of the substrate were not taken into account in the present calculations. Interaction parameters between Cu and Ni atoms have been taken as the average between the corresponding Cu-Cu and Ni-Ni hopping integrals.[28] Finally, the Cu and Ni band structures were placed on the same energy scale by aligning the Fermi energies of the two materials. In this way we avoid the difficulties of a self-consistent procedure, which in principle should be carried out to account for the influence of the charge transfer between the constituents and of the changes in the electronic configuration.[29] The validity of our assumption is confirmed *a posteriori* by the results of the calculations: No significant charge depletion is found at the surface and the fractional occupancies of the atomic orbitals are very close to the bulk values for Cu and Ni. A similar behavior has been found in calculations for bulk alloys, where this assumption has been proved satisfactory.[30]

In Fig. 2 we give the calculated local densities of states of the Cu overlayer and of the first and second atomic plane of the Ni substrate. For comparison we show in Fig. 3 the LDS of the first, second, and seventh plane of the Ni slab without the overlayers.

The LDS of the overlayer given in Fig. 2 shows two prominent structures due to the *d* states of copper. The more intense peak is located at −3.05 eV from the Fermi energy, while the other main structure is found at −4.10 eV. Notice that some structures and shoulders are present in the region between E_F and −2.5 eV, where Ni *d* states contribution is dominant. As far as the orbital composition is concerned, the two peaks include contributions of all kind of orbitals with a large amount of d_{xy} character in the peak at higher binding energy and a dominant $d_{3z^2-r^2}$ character in the main structure at −3.05 eV.

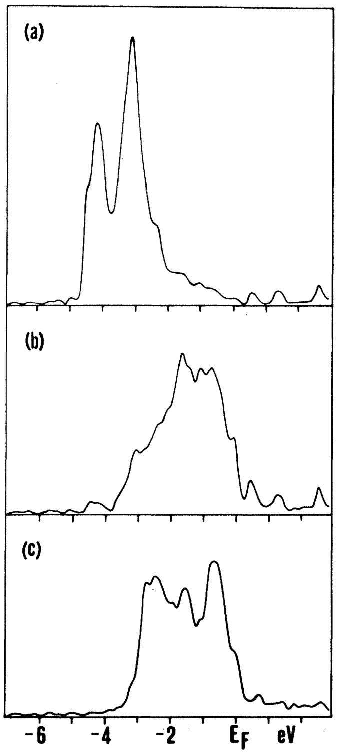

FIG. 2. Calculated local density of states (LDS) for the Cu overlayer (a) and for the first (b) and the second (c) layer of the Ni substrate. The LDS have been calculated using a mesh of 18 $\vec{k}$ points in the irreducible part of the two-dimensional Brillouin zone and convoluted with a broadening function of 0.3-eV width.

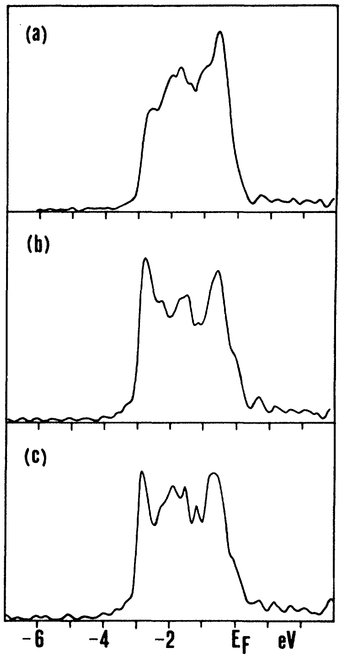

FIG. 3. Calculated LDS of Ni(111) without Cu overlayers. The results refer to the first layer (a), the second layer (b), and the seventh layer (c).

V. DISCUSSION

The discussion of the results presented in the previous sections is largely based on an interplay between theory and experiment. This comparison will be carried out in terms of initial-state calculations disregarding the matrix-element selection-rule effects and the many-body effects in the comparison between experimental EDC's and calculated LDS. This is only an approximation: The success of this scheme in the interpretation of angle-integrated photoemission from noble and transition metals[31] suggests this approach as a first approximation. The discussion concerns several points.

(i) The experimental results show clearly that the *d* band photoemission from Ni is modified by the presence of Cu on the surface. This happens at low coverages also, as it is pointed out in Fig. 4; the Ni 3*d* state modification is energy depen-

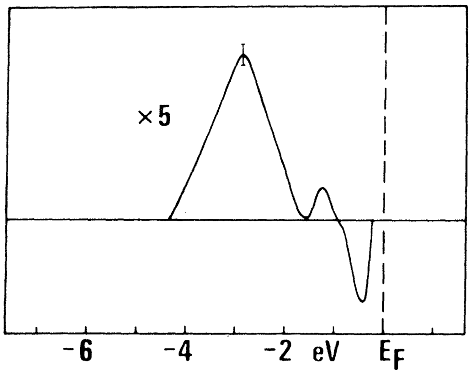

FIG. 4. Difference curve between the EDC at $\theta = 0.1$ monolayer and the EDC from Ni(111).

dent and is not due to an attenuation. This fact provides evidence of a significant interaction between the *d* states of Cu and Ni atoms. This conclusion is confirmed by the theoretical results: The LDS of the first Ni layer beneath the Cu monolayer is considerably different in the Ni 3*d* region from the LDS of the clean Ni surface given in Fig. 3. Such a result is not surprising in view of the fact that the *d*-*d* hopping integrals between Cu and Ni atoms are rather close to those of the pure metals. The excellent agreement between theory and experiment in the modifications of the Ni 3*d* emission is clearly shown in Fig. 5, where we have given the EDC's from the clean Ni(111) crystal and from the sample with one monolayer coverage of Cu together with the theoretical curves obtained by weighting the LDS of the different planes with the escape probability of photoelectrons.

(ii) The calculated *d* contribution to the Cu overlayer LDS agrees with experiment with the exception of a minor structure at higher binding energy (−4.2 eV), which is not seen in the experimental data. The measured line shows an asymmetry which could be reminiscent of this structure. In this connection we can note that the inclusion of lifetime broadening effects could make the agreement between theory and experiment closer. Similar discrepancies between photoemission data and theoretical LDS for clean Ni(111) have been interpreted as eliminated by introducing an energy-dependent broadening due to a relaxation mechanism.[32] Also, matrix-element effects could be responsible for the reduction of the emission from a high binding-energy peak. In the present experiment it was not possible to change the angle of incidence of light and to use higher photon energies in order to check this point.

(iii) Significant modifications in the Cu 3*d* line take place when different substrates are used. In the Zn(0001) case[5] the substrate behaves basically as a free-electron metal and the copper 3*d* line is found at higher binding energies. A comparison between Zn(0001) and Ni(111) data for $\theta = 1$ is given in Fig. 6. Several effects could contribute to this difference in the location of the Cu peak with respect to E_F. In the present experiment and in the previous one[5] we measured the work functions and we can say that the difference in the work function of Ni(111) and Zn(0001) cannot account for more than 0.3 eV of the measured Cu 3*d* shift. As far as the difference in relaxation energy is concerned, it is to be noted that it should be of the same order of magnitude as the shift obtained from a comparison between Cu-Ni and Cu-Zn alloys. Even in bulk alloys the Cu peak is at higher binding energies in Cu-Zn,[33-35] but the shift is accounted for by single-particle band-structure calculations.[36,37] It seems, therefore, that relaxation effects do not provide the main contribution to the measured change in the binding energy, so we will discuss it on the basis of the initial-state calculations.

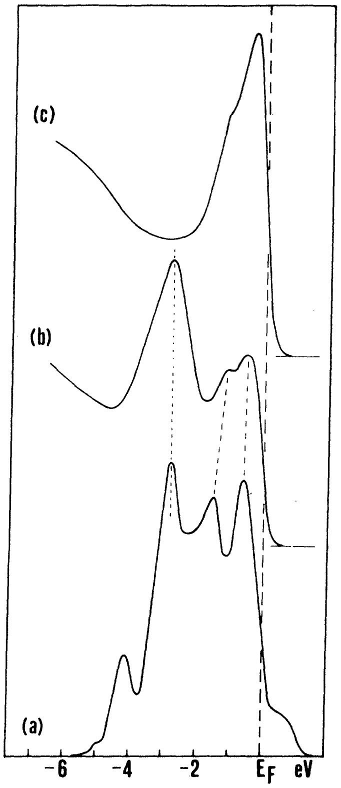

FIG. 5. Comparison between theory and experiment for one Cu monolayer on Ni(111). Calculated densities of states from the atomic planes weighted on the photoelectron escape probability (a). Measured photoemission spectrum for one monolayer coverage on Ni(111) (b). Photoemission spectrum from clean Ni(111) (c).

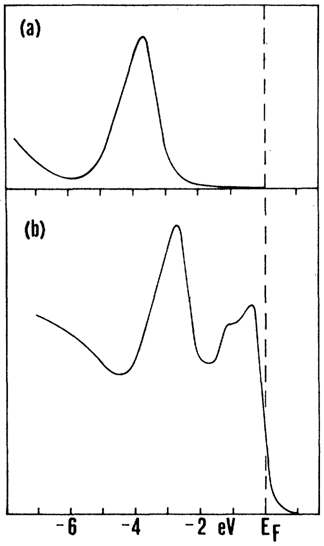

FIG. 6. Angle-integrated EDC's for (a) one Cu monolayer on Zn(0001) from Ref. 5, (b) one Cu monolayer on Ni(111).

The theoretical LDS for a Cu monolayer on Zn(0001) and Ni(111) are compared in Fig. 7. They show clearly the same trend found in the experimental results of Fig. 6. For the simple-metal substrate the shift towards higher binding energies can be understood in terms of a renormalization of *sp* orbitals caused by the decompression of charge allowed in the overlayer geometry, as discussed in Ref. 5. In the Ni case the dominant interaction which controls the position of the Cu peak is the interaction with the 3*d* states of the substrate.

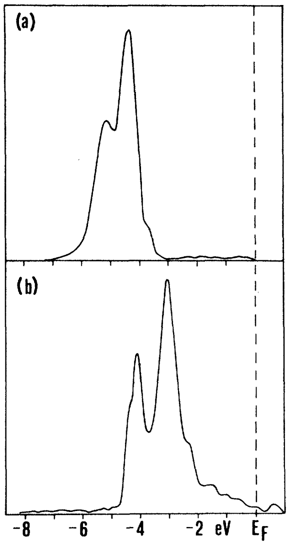

FIG. 7. Comparison between theoretical LDS's for a Cu monolayer on Zn(0001) (a) and on Ni(111) (b).

VI. COMPARISON WITH PREVIOUS WORK AND CONCLUSIONS

To the authors' knowledge theoretical results of the electronic structure of deposited Cu monolayers are not available in the literature. Most of the theoretical work has been focused on the problem of the evaluation of the density of states of an isolated monolayer. For this specific problem the results found by various authors show significant differences depending on different boundary conditions, the constraints on the charge density, and the degree of self-consistency achieved in the calculation. Both the location and shape of the *d* band are extremely sensitive to these theoretical details.

Although theoretically interesting, the results of these calculations seem not to be comparable with the experimental data for deposited overlayers. A shift of the *d* band of the Cu overlayer to lower binding energy as indicated by these calculations[11,13,14] has never been found experimentally, although several techniques have been used to study Cu deposition on different substrates. Rather, a shift to higher binding energies has been measured for those systems where the interaction of the *d* band with the substrate was not strong.[5,6] The discrepancy indicates that the change in coordination and geometry prevents meaningful comparisons between the monolayer and the overlayer case.

In the present paper, as well as in our previous work for Cu on a Zn(0001) surface, we have adopted a semiempirical approach based on a linear combination of atomic orbitals method. The method provides a simple but accurate description of the electronic properties of bulk noble and transition metals. By using the average approximation for the hopping integrals and some convenient procedure to deal with charge-transfer effects, it can be extended to the overlayer case. The approach has the disadvantage of imposing constraints on the charge density which do not allow a fully self-consistent calculation. It is therefore expected to work better in those situations where the charge-transfer effects are not too important. This appears to be the case of Cu overlayer on Zn(0001) and Ni(111) surfaces, where the method provides a reasonably accurate interpretation of the photoemission data. Note that the agreement is better for Cu on Ni, where the charge transfer is small.

Since the tight-binding parameters are taken by a fit to bulk data and the location of the *d* band of these metals is somewhat sensitive to the exchange and correlation potential even in the bulk, one should regard the theoretical description provided by the present model as only approximate. A more thorough understanding of the electronic screening at the surface and a self-consistent treatment of exchange and correlation are required for a more accurate description of these systems.

Turning to the experimental data, we note that the results of Eghelhoff and Tibbets[6] on Cu deposited on carbon confirm the conclusions of our discussion. In analogy with the Cu on Zn(0001) case, the Cu 3*d* peak of the overlayer is shifted toward higher binding energy and the shift increases at low coverages ($\theta < 1$), where almost isolated atoms of Cu are present on the substrate.

It is interesting to compare our results with the large amount of experimental information published on Cu-Ni alloys.[35,38-40] The position of the Cu 3*d* band is found in these experiments almost at the same energy as in our case (in particular for low Cu concentrations of the alloys). A situation closely similar to that found in our experiments occurs in the Cu-Ni alloys, where copper segregation at the surface strongly enriches in Cu the outermost plane.[41] A comparison of our data with those of Ref. 35 shows that the main features are located at nearly the same energy in both cases, but the Ni 3*d* peak is less structured in the alloy than in the overlayer case. Also, the Cu peak is considerably wider in the alloy case. These differences are probably a consequence of a better regularity of the overlayer case with respect to the enriched surface of the alloy.

In conclusion, we have presented two major results. We have given the experimental evidence of the fact that the electron states of Cu on Ni(111) depend strongly upon the *d*-*d* interaction between the adatoms and the substrate; this is also the case of the Cu monolayer whose electronic structure varies markedly when it interacts with a transition-metal substrate or with a simple metal.

Secondly, we have shown that in both cases it is possible to account satisfactorily for the main features of the experimental results with a simple theoretical description.

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[1] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 30, 177 (1973).

[2] D. M. Kolb, D. Leutloff, and M. Przasnysky, Surf. Sci. 47, 622 (1975).

[3] K. S. Liang, W. R. Salanek, and I. A. Aksay, Solid State Commun. 19, 329 (1976).

[4] P. Heimann, H. Neddermayer, and H. F. Roloff, in *Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces* (IVC, ICSS, Vienna, 1977), p. 2145.

[5] I. Abbati, L. Braicovich, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. Lett. 40, 469 (1978).

[6] W. F. Egeloff and G. G. Tibbets, Phys. Rev. B 19, 5028 (1979).

[7] B. R. Cooper, Phys. Rev. Lett. 30, 1316 (1973).

[8] S. J. Gurman, J. Phys. F 5, L194 (1975).

[9] J. G. Gay, J. R. Smith, and J. F. Arlinghaus, Phys. Rev. Lett. 38, 561 (1977).

[10] C. M. Bertoni, O. Bisi, C. Calandra, and F. Manghi, Thin Solid Films 43, 251 (1977).

[11] G. S. Painter, Phys. Rev. B 17, 3848 (1978).

[12] J. A. Appelbaum and R. D. Hamann, Solid State Commun. 27, 881 (1978).

[13] C. S. Wang and A. J. Freeman, Phys. Rev. B 18, 1714 (1978).

[14] F. J. Arlinghaus, J. G. Gay, and J. R. Smith, Phys. Rev. B 20, 1332 (1979).

[15] M. Metha and C. S. Fadley, Phys. Rev. Lett. 39, 1569 (1977).

[16] K. S. Sohn, D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 13, 1515 (1976); 14, 3185 (1976).

[17] C. M. Bertoni, O. Bisi, C. Calandra, F. Nizzoli, and G. Santoro, J. Phys. F 6, L41 (1976).

[18] I. Abbati, L. Braicovich, and A. Fasana, unpublished.

[19] S. Shirai, Y. Fukuda, and N. Nomura, J. Phys. Soc. Jpn. 16, 1989 (1961).

[20] A. Chambers and D. C. Jackson, Philos. Mag. 31, 1357 (1975).

[21] J. E. Demuth, Surf. Sci. 69, 365 (1977).

[22] I. Lindau and W. E. Spicer, J. Electron. Spectrosc. 3, 409 (1974); see also C. R. Brundle, Surf. Sci. 48, 99 (1975).

[23] H. P. Bonzel and E. E. Latta, in *Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces* (IVC, ICSS, Vienna, 1977), p. 1221.

[24] E. E. Latta and H. P. Bonzel, Phys. Rev. Lett. 38, 839 (1977).

[25] J. C. Slater and C. Koster, Phys. Rev. 94, 1498 (1954).

[26] G. A. Burdik, Phys. Rev. 129, 138 (1963).

[27] C. S. Wang and J. Callaway, Phys. Rev. B 15, 298 (1977).

[28] H. Fukujama, H. Kralauer, and L. Schwartz, Phys. Rev. B 10, 1173 (1974).

[29] C. D. Gellatt and H. Ehrenreich, Phys. Rev. B 10, 398 (1974).

[30] H. Ehrenreich and L. M. Schwartz, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31, p. 150.

[31] N. V. Smith, Phys. Rev. B 9, 1365 (1974).

[32] J. B. Pendry and J. L. F. Hopkinson, J. Phys. F 8, 1009 (1978).

[33] P. O. Nillson and I. Lindau, J. Phys. F 1, 854 (1971).

[34] P. T. Andrews and L. A. Hisscott, J. Phys. F 5, 1568 (1975).

[35] K. Y. Yu, C. R. Helms, W. E. Spicer, and P. W. Chye, Phys. Rev. B 15, 1629 (1977).

[36] V. L. Moruzzi, A. R. Williams, and J. F. Janak, Phys. Rev. B 9, 3316 (1974).

[37] G. M. Stocks, R. W. Williams, and J. S. Faulkner, Phys. Rev. B 4, 4390 (1971).

[38] S. Hufner, G. K. Wertheim, R. L. Cohen, and J. H. Wernick, Phys. Rev. Lett. 28, 488 (1972).

[39] N. J. Schevchik and C. M. Penchina, Phys. Status Solidi B 70, 619 (1975).

[40] P. Heimann, H. Neddermayer, and M. Pessa, Phys. Rev. B 17, 427 (1978).

[41] Y. S. Ng, T. T. Tsong, and S. B. McLane Jr., Phys. Rev. Lett. 42, 588 (1979).