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Self-consistent local-orbital calculation of the surface electronic structure of Ni (100)

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The electronic structure of the Ni (100) surface has been calculated fully self-consistently. The calculation predicts markedly fewer surface-state (surface-resonance) bands than our previous Cu (100) calculation. In all other aspects, the Ni (100) and Cu (100) surface electronic structures are very similar.

The surface electronic structure of nickel is one of the most active fields of study at present. Chemisorption studies on nickel surfaces are probably more plentiful than on any other metal, and the magnetic properties of nickel present many still lively controversies. Thus nickel is a very interesting metal for theoretical study.

Heimann and Neddermeyer[1] report a surface state on Ni (110), and Page *et al.*[2] have seen one on evaporated nickel. Clean nickel surfaces have aroused great interest recently due to the controversy over magnetic "dead layers" at the surface and over the question of spin-polarization reversal near the surface. Eib and Alvarado[3] observed that the spin polarization of photoemitted electrons from Ni (100) changed sign 0.1 eV above threshold. Dempsey, Grise, and Kleinman[4] attribute this to a surface state near the zone center just below the Fermi energy, while Himpsel *et al.*[5] argue that no surface state is needed because the exchange splitting at the Γ point is ~ 0.1 eV. Moore and Pendry[6] calculate the spin-polarized photoemission from nickel using a one-electron theory and find good agreement with Eib and Alvarado's experiment.[3] Moore and Pendry find they can explain the experimental results without forcing surface states to appear.

Himpsel and Eastman[7] observe a surface state on Ni (111) near the zone center, but their placement of bands does not agree with the bulk-band-structure calculations of Callaway.[8] More recently, Plummer and Eberhardt[9] have observed a Ni (100) surface state which is magnetic, due to the spin splitting.

We have previously calculated the surface electronic structure of the (100) surface of copper[10] and nickel[11] using a three-layer-slab model. Recently we have extended this work to a nine-layer-thick Cu (100) slab[12] which is thick enough to allow us to distinguish surface states. A large density-of-surface state was predicted for Cu (100). Subsequently a predicted[12] surface-state band was seen experimentally[13] on Cu (100). The measured energy dispersion of the surface-state band was in close agreement with our theoretical prediction.[12] It is natural also to extend the Ni (100) calculation to a nine-layer slab, especially in light of the tremendous current interest in nickel.

The self-consistent local-orbital technique is described in detail elsewhere.[14] We use as the basis set all the core and valence orbitals of atomic nickel, plus $4p$, $4d$, and $5s$ excited-state orbitals to provide additional variational freedom. The core-charge density is "frozen" at its atomic value. This charge density and the atomic orbitals are computed by a Herman-Skillman type calculation.[15] The orbitals are fit using a series of Gaussians. We use a local-density exchange-correlation approximation derived from the Wigner interpolation formula for both the atomic and solid-state calculations. Thus we treat nickel paramagnetically.

Starting matrix elements are computed in direct space. We compute the electronic structure and charge density at 3 $k_{\parallel}$ points in the elemental $\frac{1}{8}$ of the surface Brillouin zone, using a special points scheme,[16] and we iterate our solutions to self-consistency. The self-consistency corrections are computed entirely in reciprocal space, using Fourier-transform methods. As a consequence, there are no constraints on the shape of the final self-consistent potential. To indicate the quality of the calculation, we note that it is self-consistent to within 50 meV everywhere in the slab and yields a work function of 5.1 eV, which is in excellent agreement with experiment. The measurements of Eib and Alvarado[3] yielded 5.2 eV for the Ni (100) work function, while Papageorgopoulos and Chen[17] reported 4.95 eV, both results being within 0.1 eV of our theoretical value.

After the self-consistent solutions have been determined, the electronic structure of the Ni (100) slab is computed at 45 uniformly spaced points in the elementary $\frac{1}{8}$ of the surface Brillouin zone. These solutions are used to compute electronic densities of states and to display the energy bands of the slab.

We begin by showing in Fig. 1 the effect of slab thickness on the Ni (100) results. The total density of states (TDOS) is displayed as a function of energy

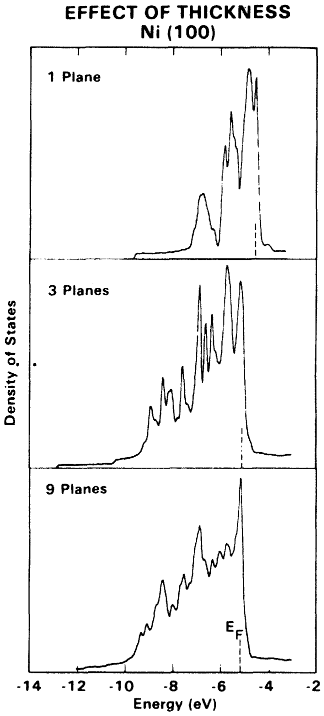

FIG. 1. Total density of states for one-, three-, and nine-plane models of Ni (100).

for slabs one-, three-, and nine-planes thick. The general character of these results is much the same as previously noted for Cu (100).[12,14] There is little change in going from three to nine planes, but the one-plane results are, not suprisingly, a good deal different. The work function is not at all sensitive to film thickness—5.1 eV is the work function for both three and nine planes, and the one-plane value is 4.7 eV, not a great deal different. The agreement of the work-function values for three and nine planes is presumably due in part to the relatively short screening lengths found in metals. That is, even a three-layer film has a bulklike charge density in the region around its central plane.[10] In the case of Cu (100), we found a 4.5-eV work function for three, five, seven, and nine layers, again within 0.1 eV of experiment for thick films.[12]

The width of the Ni (100) *d* band is also the same for both three and nine planes. The one-plane *d* band is much narrower with a second moment only $\frac{2}{3}$ as large. This is again not surprising, since naive tight-binding theory would predict it because each nickel atom in the Ni (100) monolayer has far fewer nearest neighbors than in the bulk or in the interior of a thicker film.

The principal difference on going from three to nine layers is the elimination of the sharp spikes in the total density of states. The nine-layer TDOS is smoother and has fewer prominent peaks. Nevertheless, there is little real difference between the three- and nine-layer curves, in agreement with conclusions previously reached for Cu (100).[12] It is apparent that, as for Cu (100), a five-layer film would probably be adequate insofar as the total density of states represents the physical results. Our motivation in using a nine-layer film is, again as for Cu (100), to search for surface states. A three- or five-layer-thick film is just not thick enough to make apparent the localization of an electron state in the surface region. For this single but important reason we were compelled to use the nine-layer film.

We turn now to a detailed discussion of the nine-layer-slab results. In Fig. 2 we compare the calculated total density of states for Ni (100) with the x-ray photoemission data of Kowalczyk.[18] There is general agreement between the two curves, although the calculated curve is wider. It is necessary to note further the similarities and differences between these results for Ni (100) and the nine-layer-Cu (100) results.[12,14] We wish to make a number of such comparisons as we discuss the Ni (100) results. Here we note the great similarity in the density-of-states curves for the two materials. The only great qualitative difference is, in fact, the position of the Fermi level which, of course, for nickel falls within the *d* band near the top edge rather than 1.5 eV above as for copper. Otherwise, the similarity is striking.

Most theoretical density-of-states curves for nickel are wider than experiment and ours is no exception. This is a curious result, since copper and nickel are so similar in general. Theoretical results are usually also similar for copper and nickel. The disagreement between theory and experiment for nickel is anomalous and no full explanation is available. A difference in hole

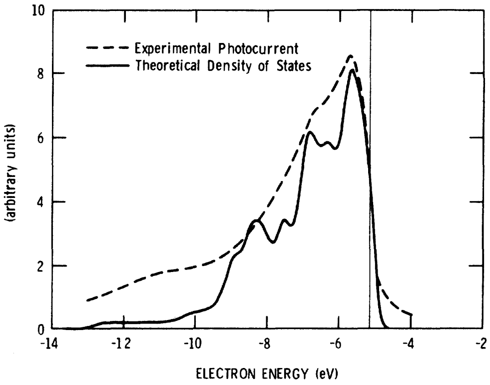

FIG. 2. Theoretical TDOS for Ni (100) compared to x-ray photoemission signal.

lifetimes for the photoemission process has been suggested as the explanation.[19] The present calculation does not resolve this problem; our results are, however, quite in line with other theoretical work.

In Fig. 3 we show the Ni (100) charge density as a contour plot in a (110) plane perpendicular to the surface of the slab. This figure is virtually indistinguishable from that for Cu (100), and similar statements apply. The charge is quite spherical around the atomic sites; the disturbance due to the presence of the surface is not noticeable beyond the second atomic layer, and the charge density "heals" and becomes very smooth only a short distance out into the vacuum.

The local density-of-states curves for the nine-layer-Ni (100) slab are set out in Fig. 4. At the top is the total density-of-states curve, followed by the local-density-of-states (LDOS) curves for the central plane of the slab, the second plane from the surface (i.e., the fourth plane from the center), and the surface plane. These LDOS curves are derived by projecting the total density on the appropriate orbital components of the calculated wave functions with cross terms divided equally between their two components in the Mulliken fashion. The second and third plane LDOS curves (numbering from the center outward) are not shown, since they are indistinguishable from that of the central plane.

The central plane LDOS is very similar to the total density, which indicates that we have a substantial bulklike interior region, and that the nine layers form an adequate representation of the surface and bulk regions. It is also to be noted that all seven interior planes are essentially identical, although some differences in peak heights are evident in the second layer from the surface. This is again evidence that the effect of the surface's presence is confined to the surface layer with essentially no discernible disturbance further into the solid.

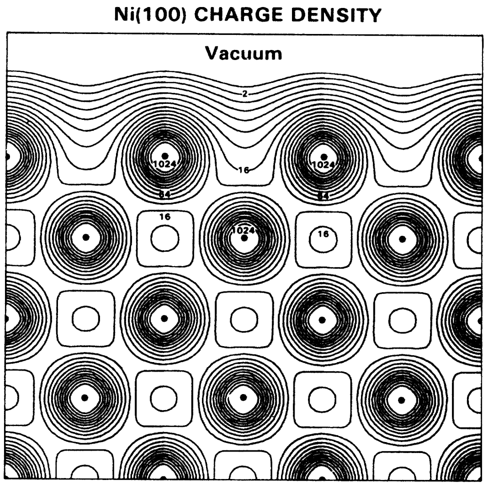

FIG. 3. Ni (100) charge density plotted in a (110) plane perpendicular to the nine-plane slab and passing through the center of the atoms.

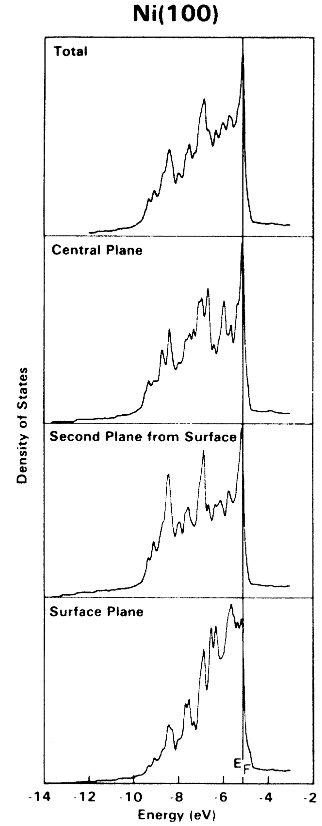

FIG. 4. Ni (100) total density of states and planar density of states for central plane, second plane from the surface, and the surface plane.

However, while the second layer is very much like the central layer, the surface layer LDOS is dramatically different. There is an obvious narrowing of the nickel d band at the surface; its second moment is reduced to $\frac{2}{3}$ of its value for the other planes. This narrowing is perhaps not so dramatic as was the case for Cu (100), but it is there nonetheless. There is also an enhancement of the surface LDOS over the inner plane LDOS, particularly in the ~1 eV below E_F. Here again the enhancement is much less dramatic than in the Cu (100) case.

In Fig. 5 we show a plot of the surface band structure for Ni (100). The principal features, already evident from the DOS curves, are the broad s-p bands which cover the entire energy range of the figure, and the narrower (~4-eV-wide) Ni d bands cutting across the wide s-p bands. The

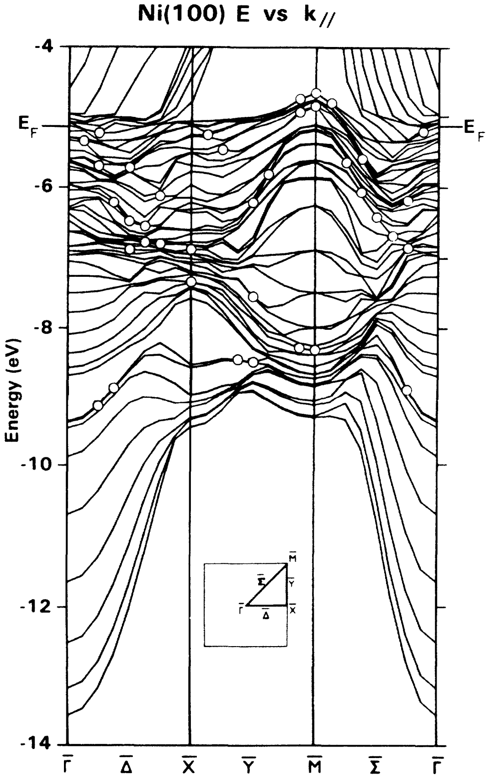

FIG. 5. Two-dimensional energy bands along the high-symmetry directions for the nine-plane Ni (100) slab. The open circles represent the surface states on a 45-k-point mesh.

Fermi energy lies within the d bands very near the top edge. On this plot the surface states we have found are marked by the open circles.

A surface state is an eigenstate of the system in which the electron is confined to the surface region and avoids the bulk. Operationally, for our nine-layer-slab representation of the surface, surface states may be defined as states that exist primarily on the outer planes of the slab and thus essentially avoid the central planes. Accordingly, in Fig. 5 a state is called a surface state (or surface resonance) if more than 80% of its probability density is located on the outer two planes at each surface. We see a number of such states in Fig. 5, scattered throughout the nickel d band.

Unlike the Cu (100) case, there are far fewer such surface states in Ni (100), and they are not concentrated in any one energy interval. In Fig. 6, we plot the charge density due to the sum of all the occupied Ni (100) surface states from Fig. 5. The contour plot on the right shows that they truly are surface states, that the charge density dies quickly away from the surface. The complicated angular dependence evident on the left-hand side of the plot demonstrates the d-like character of these states. The angular dependence varies from plane to plane, which, of course, would not be true of a bulk state.

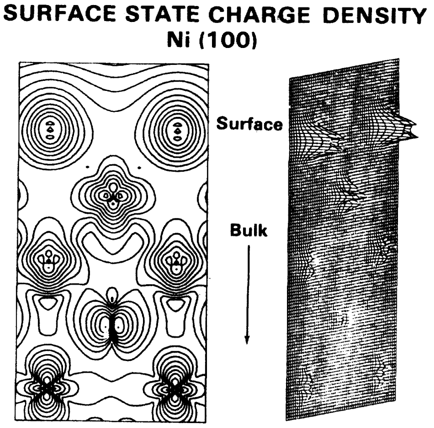

FIG. 6. Charge density of all Ni (100) occupied surface states.

It is remarkable how similar the electronic structure of Ni (100) is to that of Cu (100). The various features of the Ni (100) electronic structure which have been enumerated here are all very similar to the same features of Cu (100). These similarities have been noted one by one throughout this paper. To summarize: we note the charge density in Fig. 3, virtually identical to that of Cu (100); the local-density-of-states curves in Fig. 4, which are the same in all essentials and quite similar in detail to those of Cu (100); and the surface band structure in Fig. 5. The only obvious difference is the placement of the Fermi energy.

When we come to the question of surface states, however, the difference is profound. There was a strikingly large density of surface states in Cu (100), heavily concentrated at the top edge of the copper d band. In Ni (100), the number of surface states is modest, and they are fairly evenly distributed. This lack of concentration will make the Ni (100) surface states difficult to observe in the presence of the large number of bulk states.

Plummer and Eberhardt[9] have in fact observed surface states on Ni (100) in recent angular-resolved photoemission experiments. They find a narrow, surface-sensitive peak at the Fermi energy, which might correspond to our predicted surface states at $\bar{M}$. These are empty states but might become filled for majority-spin bands if we added spin splitting to our calculation. Plummer and Eberhardt claim their observed state is "magnetic," that is, due to a gap in one spin band but not in the other.

As our calculation is strictly paramagnetic, it can obviously say nothing about any effect which is specifically due to the presence of spin splitting and two sets of bands. However, Wang and Freeman[20] find almost identical sets of surface states for spin-up and spin-down bands. This would indicate that our paramagnetic results are in fact quite relevant, and that the magnetic effects are incidental to the question of surface states. Others have seen evidence of nonmagnetic surface states on the (111) surface of nickel,[7] but not on the (100) surface. Finally, recent photoemission results of Hagstrum[21] show no clear evidence of a significant surface-state density on Ni (100). Thus the question of experimental verification of our Ni (100) surface states remains open. This is the first fully self-consistent nickel surface calculation and will be important to the extent that magnetic effects are not controlling.

We are still left with the question of why the Ni (100) and Cu (100) surfaces differ so much with respect to surface states. It would appear that copper exhibits a reasonable number of surface states, while nickel exhibits an uncommonly small number. Two possible rationales occur to one at once. Either we find few surface states because we have left out the spin splitting, or the occurrence of the Fermi energy within the d band makes conditions unfavorable to their existence. These are not entirely distinct possibilities, as spin-polarized nickel would have one full subband and one partially filled, and the filled-subband case would be similar to copper. Wang and Freeman[20] find results similar to ours in a ferromagnetic Ni (100) calculation with relatively few surface states. This suggests that the spin splitting is not the critical factor, although this is far from conclusive. Perhaps more important, however, is the likely effect of the location of the Fermi energy within the d band on the self-consistent surface potential. If one were to move the Fermi energy of copper down to its position in nickel, roughly half of the copper surface states would empty. This would significantly change the self-consistent potential in the vicinity of the surface states. As it was found[12] that the high density of surface states split off from the upper d-band edge in Cu (100) were sensitive to self-consistency, this conceivably is the explanation for the difference in the nickel and copper results. We are compelled to say that this interesting question must remain unsettled until more theoretical and experimental work can be done. We are particularly eager to see such results for a wide variety of metals. Only such work and the careful cross correlating of the results for various metals will serve to settle this question in the end.

Note added in proof. We have recently completed self-consistent local orbital calculations of the surface electronic structure of Pd (100) and Ag (100). The number of surface states we found on each of those two metals is comparable to the number we found on Cu (100), and larger than that which we found on Ni (100).

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[1] P. Heimann and H. Neddermeyer, J. Phys. F 6, L257 (1976).

[2] P. J. Page, D. L. Trimm, and P. M. Williams, J. Chem. Soc. Faraday Trans. 1, 70, 1769 (1974).

[3] W. Eib and S. F. Alvarado, Phys. Rev. Lett. 37, 444 (1976).

[4] D. G. Dempsey, W. R. Grise, and L. Kleinman, Phys. Rev. B 18, 1270 (1978).

[5] F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B 19, 2919 (1979).

[6] I. D. Moore and J. B. Pendry, J. Phys. C 11, 4615 (1978).

[7] F. J. Himpsel and D. E. Eastman, Phys. Rev. Lett. 41, 507 (1978).

[8] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

[9] E. W. Plummer and W. Eberhardt, Phys. Rev. B 20, 1444 (1979).

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

[11] J. R Smith, F. J. Arlinghaus and J. G. Gay, Inst. Phys. Conf. Ser. 39, 303 (1978), Chap. 5.

[12] J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 42, 332 (1979).

[13] P. Heimann, J. Hermanson, H. Moisga, and H. Neddermeyer, Phys. Rev. Lett. 42, 1782 (1979).

[14] J. R. Smith, J. G. Gay, and F. J. Arlinghaus, Phys. Rev. B 21, 2201 (1980).

[15] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[16] D. J. Chadi and M. L. Cohen, Phys. Rev. B 7, 692 (1973), and 8, 5757 (1973).

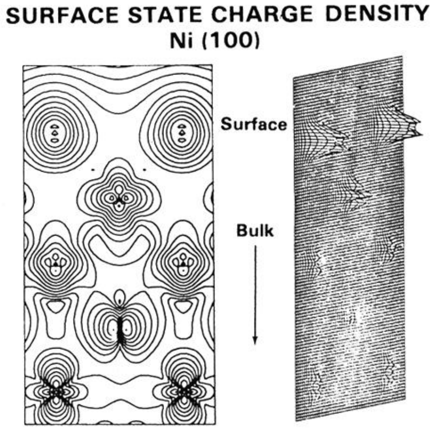
[17] C. A. Papageorgopoulos and J. M. Chen, Surf. Sci. 52, 40 (1975).

[18] S. P. Kowalczyk, LBL Report No. 4319, 1976, Ph.D. thesis, University of California, Berkeley, 1976 (unpublished).

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

[20] C. S. Wang and A. J. Freeman, J. Appl. Phys. 50, 1940 (1979).

[21] H. D. Hagstrum (private communication).



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