

Surface electronic structure of alloys with split d bands

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Semiempirical tight-binding self-consistent calculations were performed for transition-metal alloy nonpolar surfaces: $MTi(011)$ and $M_3Ti(111)$ ($M = Ni, Pd, Pt$). For both kinds of surfaces we find two occupied surface-state bands which appear due to the surface-potential shift and should be accompanied by a negative surface core-level shift for the M atoms. For the Ti atoms we find a surface state at the Fermi energy for $M_3Ti(111)$ faces without any need for the surface-potential change. For $MTi(011)$ an analogous surface feature is not well separated from the bulk states.

I. INTRODUCTION

Surfaces and interfaces of bimetallic systems can show unique physical and chemical (catalytic, magnetic, etc.) properties. Much attention has been paid to metallic overlayers on metal substrates.¹ Another important family are surfaces of transition- and noble-metal alloys and intermetallic compounds.² Since the number of examples of interface alloy formation is still growing, the boundary between these systems is not sharp.

The key to understanding the relevant phenomena is the surface electronic structure. For alloys of two similar metals or for alloys with a low concentration of the second component, the electronic structure is often related to that of the pure metal. Generally, however, features specific for a particular class of alloys can be anticipated. Unfortunately, the results in this area are scarce. It has been demonstrated that surface or interface states in the local density of electronic states (LDOS) at the Fermi energy E_F can enhance the catalytic activity of surface atoms, whereas a drop in the LDOS has an opposite effect.¹ Let us mention NiAl as an example of an alloy for which the surface states were studied extensively.^{3,4} Another quantity important for both bulk and surface atoms⁵ is the core-level shift (CLS). An interesting and nontrivial question about a possible correlation between surface states and CLS's at transition-metal-carbide surfaces was considered in Ref. 6.

Recently, we have performed self-consistent (SCF) semiempirical calculations⁷⁻⁹ of bulk and surface properties of metal alloys with split d bands MTi and M_3Ti , respectively, $M = Ni, Pd, Pt$. Starting from the initial-state interpretation of the CLS, considerable positive shifts (shifts to higher binding energies) for all atoms were found in semiquantitative agreement with the available experiments for the bulk. Besides that, we found features in the surface LDOS that could indicate the existence of surface states. In the present paper we study these problems in more detail in the light of ideas mentioned above. We consider the nonpolar (011) surface of the MTi alloy in the CsCl ($B2$) phase and the nonpolar (111) termination of the M_3Ti alloy with the Cu_3Au ($L1_2$) structure. The latter geometry is commonly used

as an approximation to the long-period phases such as DO_{24} for Pd_3Ti . A comment is necessary concerning the ideal surface termination assumed below. Although reconstructions and especially segregation are common at alloy surfaces, the ideal (1×1) surfaces are frequent as well. With regard to the lack of experimental data,² the study of ideal structures is a useful first step and the results are of more general methodical interest. It is possible that rippled relaxations¹⁰ which do not destroy the (1×1) geometry are present at many alloy and compound surfaces. Actually, we studied a kind of rippled termination in Pd-Ti systems^{7,8} by assuming the surface-subsurface bond lengths to obey the Vegard law and we found only negligible changes.

To close this section, let us describe the method of calculation; the reader can consult Refs. 7-9 for details. We employ the d -band semiempirical tight-binding model and calculate the LDOS by the standard recursion method. To this goal, 12 moments of the Hamiltonian are evaluated. The d -orbital quasiatomic levels (on-site Hamiltonian matrix elements) ϵ_i at site i are computed self-consistently to maintain the local charge neutrality. The change (with respect to the bulk atom in the parent metal) $-\delta(\epsilon_i - E_F)$ is identified with the CLS. It is assumed that, starting from the fourth layer, ϵ_i 's acquire the bulk values. For elemental fcc metals and for the fcc-like M_3Ti alloys, the universal d -band parameters of Pettifor¹¹ are scaled to fit the literature data on bandwidths. The only difference from the earlier calculation⁹ is that now we utilize the rescaled tungsten parameters of Ref. 12 for the bcc-like CsCl crystals. The latter parameters describe the interaction between second-nearest neighbors more correctly and yield a better LDOS for both bulk and surfaces of pure bcc transition metals. The changes introduced by the new parametrization are moderate. In particular, we display in Table I the calculated bulk and surface CLS's. Comparison with the table of Ref. 9 reveals that CLS's for MTi alloys get slightly reduced (for M_3Ti there is no change) and perhaps they are closer to experimental values quoted in Ref. 9. We have also considered the possibility of a slight ionicity in the alloys.⁹ It appears, however, that this effect has little influence on features studied below.

II. METHOD COMMENTS

In this section we briefly touch upon the topics of central interest in our study: CLS's and surface states, respectively. Despite the outstanding role the CLS measurements play, a reliable interpretation is still missing (the reader is referred to Refs. 5–9). Supposing that the hole screening in the final state in extended systems depends only weakly on the local geometry,¹³ the CLS evaluation reduces to initial-state effects. Simplifying the picture further by assuming that the highest core-level electrons and *d* electrons in transition-metal atoms experience roughly the same local change of the electrostatic potential, we arrive at the expression for CLS presented in the Introduction.

The theory of surface states on elemental solid surfaces is more or less settled.^{14–15} The Tamm surface states can split off from quasi-isolated energy bands if a sufficient surface-potential change takes place. The mechanism is effective for narrow flat bands in late transition and noble metals. Moreover, there is a clear correlation between the surface CLS resulting from the surface-potential change and Tamm states in these metals.⁶ The Shockley (or crystal-induced) states exist in hybridizational (or inverted) gaps due to hybridization effects. At alloy and compound surfaces, an intermediate kind of state can be found in the dip or gap dividing the energy bands related to different types of atoms.^{14,16} The hybridization prefers the Shockley mechanism, whereas the energy separation between the bands opposes this trend. As a result, either surface states lie near the band edge without any need of the surface-potential change, or a moderate change is sufficient to produce them. For nonpolar surfaces the potential shifts are not large and the existence of surface states (heteroatomic surface states in the terminology of Ref. 14) near the band edges is possible although not obvious. For polar surfaces, the surface-potential shifts can be large.¹⁷ In analogy to Tamm states, the question about the relation between surface CLS's and heteroatomic states arises.⁶ In theoretical papers,^{6,18} several surface-state bands were predicted for the TiC (001) face accompanied by no surface CLS on carbon atoms. In Ref. 17 similar results were arrived at by postulating small changes of the surface potential. Hence, for heteroatomic surfaces there are still some subtle points (such as the CLS–potential relation) to be clarified.¹⁶

To resolve the surface-state features in the LDOS, the analysis of states corresponding to different points of the surface Brillouin zone is most convenient. Such an analysis is not available within our recursion-scheme study. We shall give a simple result helpful in the subsequent discussion. Namely, if for the LDOS $n(E)$ the inequality

$$2n_b(E) < n_s(E) \quad (1)$$

holds (the indices *b* and *s* refer to the bulk and surface, respectively), the semi-infinite crystal wave function for the energy E cannot be derived from bulk states solely. We sketch only a simplified proof of this statement. Denoting by n the number of the atomic layer parallel to

TABLE I. Calculated core-level shifts (CLS) at bulk (b) and surface (s) atoms in MTi and M_3Ti alloys. The shifts are taken with respect to the bulk atom in the corresponding elemental metal.

System	CLS (eV)			
	M_b	M_s	Ti _b	Ti _s
NiTi	0.64	0.35	0.74	0.89
PdTi	1.73	1.20	0.82	0.92
PtTi	0.51	0.11	0.99	1.07
Ni ₃ Ti	0.23	−0.01	1.26	1.32
Pd ₃ Ti	0.92	0.49	1.57	1.48
Pt ₃ Ti	0.24	−0.12	1.47	1.43

the surface and by K the wave-vector component perpendicular to it, we find for bulk states with the energy $E = E(K)$ two independent solutions of type $\phi_1 = \cos Kn$, $\phi_2 = \sin Kn$. For the LDOS we obtain $n_b(E) = (\phi_1^2 + \phi_2^2)n(E) = n(E)$. Supposing that for the semi-infinite crystal occupying the half-space $n \geq 0$ the wave function is a linear combination of bulk solutions, we write $\phi_s = (2)^{1/2} \cos[Kn + \delta(K)]$. The factor $(2)^{1/2}$ is introduced to maintain the normalization when summations are restricted to the half-space only. The identity

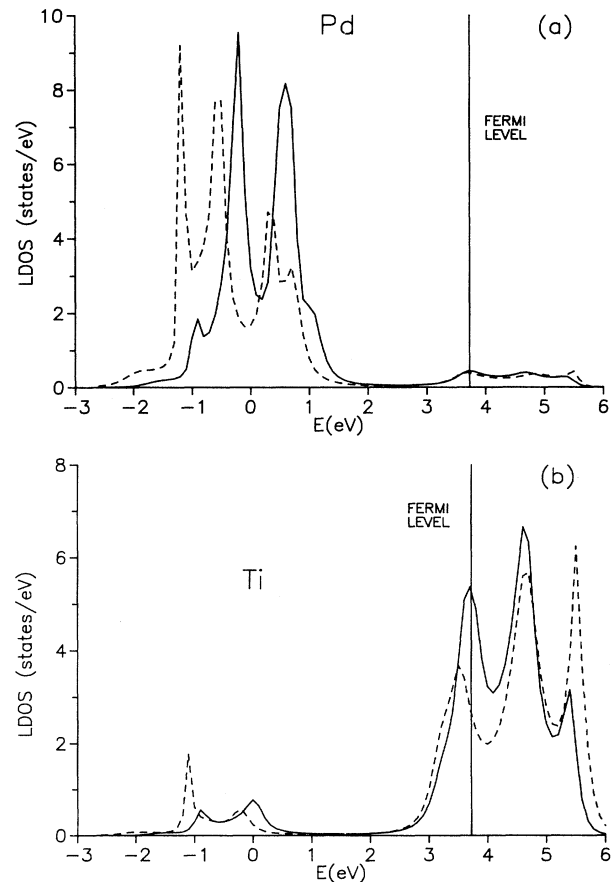


FIG. 1. The local density of electronic states (LDOS) for the PdTi alloy at the (011) surface (solid line) and in the bulk (dashed line), respectively. Results are shown for Pd atoms (a) and Ti atoms (b).

$n_s(E) = \phi_s^2(n=0)n(E)$ proves the conjecture. The criterion (1) is a sufficient condition for the surface state (resonance) existence and the factor 2 is generally too severe. Nevertheless, it allows us an identification of some surface states in the next paragraph.

III. RESULTS AND DISCUSSION

The band-structure calculations^{19,20} for MTi and M_3Ti alloys, respectively, show essentially filled M bands divided from partly occupied Ti bands by a dip (quasigap) in the LDOS. There are also several flat d bands giving rise to peaks in the LDOS. Let us consider now the surface-potential shifts and the related CLS's as predicted in our calculations. To conform with the standard definition (shifts with respect to bulk atoms in the same crystal) we must subtract the bulk values given in Table I from the surface ones (cf. Ref. 9). For M atoms the surface CLS's are 0.2–0.5 eV towards lower binding energies, similarly as for the corresponding pure metals. For Ti atoms small surface shifts about 0.1 eV of either sign result. In the light of the preceding discussion two kinds of surface

states can appear: (i) Tamm states of M character induced by the surface-potential shift, and (ii) heteroatomic states of M or Ti character near the LDOS dip boundaries.

It appears that for the three cases $M = Ni, Pd,$ and Pt the results are similar and it is sufficient to give several illustrations (for Pd_3Ti see Ref. 8). To understand the surface-potential role in the surface-state formation, we have repeated the calculations with the bulk values of ϵ_i fixed for all atoms in the semi-infinite crystal. (The reader might notice small differences in the bulk LDOS shown below for surface-SCF and non-SCF calculations, respectively. As explained above, our bulk results refer actually to the fourth subsurface layer, which feels to a degree the difference between the surface-SCF and non-SCF potentials.)

For the $PdTi$ (011) surface [Fig. 1(a)] we find a Tamm state in the central dip in the bulk Pd LDOS (at 4 eV below E_F) and another surface feature at the top of the Pd bands (at 3 eV below E_F). The criterion (1) is helpful here. It is arbitrary whether we classify the upper peak as a Tamm or potential-induced heteroatomic state. Comparison with the non-SCF LDOS [Fig. 2(a)] proves clearly the link between the CLS and the two surface-state peaks. (At band edges the three-dimensional Van Hove singularities have low-density square-root character and the peaks in the bulk LDOS must come from inner

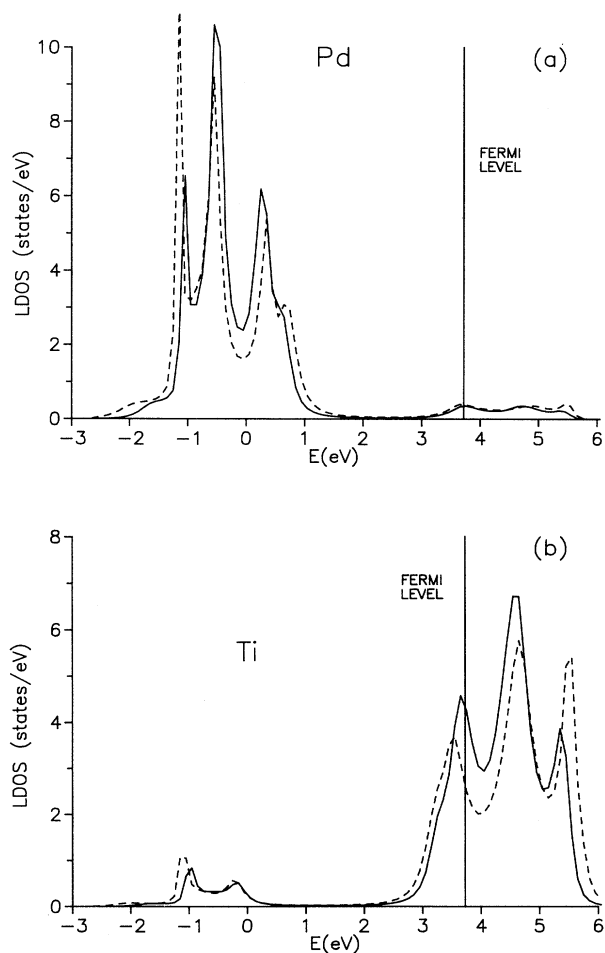


FIG. 2. The same as in Fig. 1. The surface–non-self-consistent (non-SCF) results are shown.

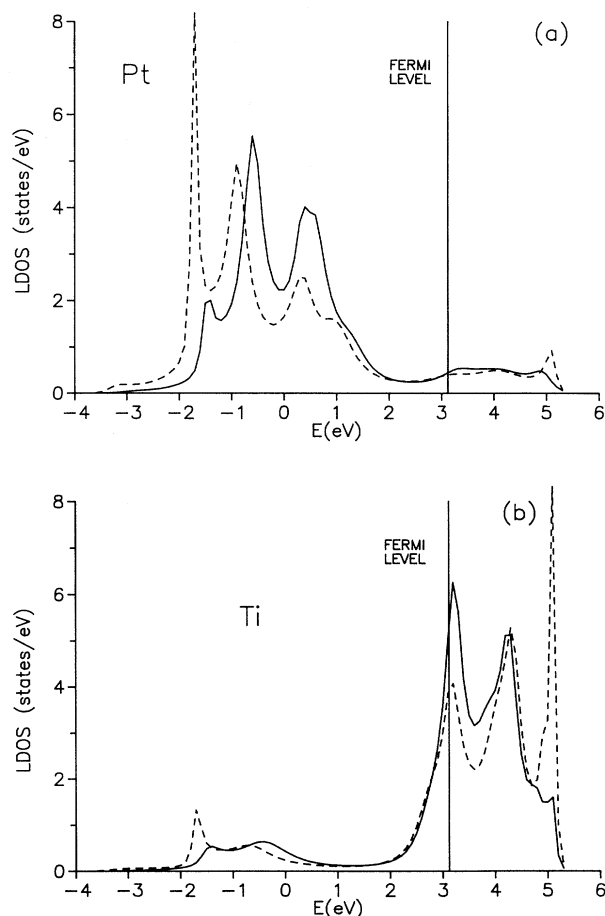


FIG. 3. LDOS for the $PtTi$ alloy. See Fig. 1 for details.

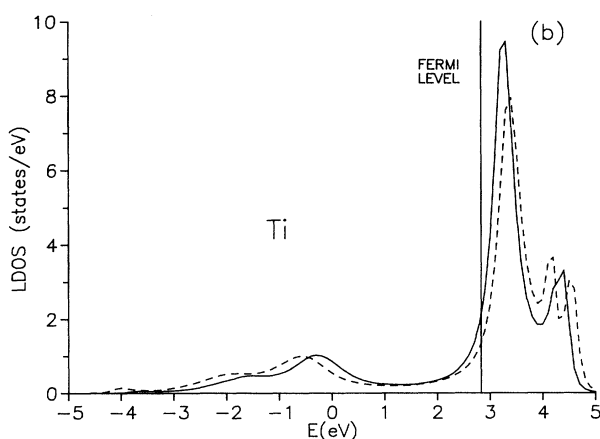
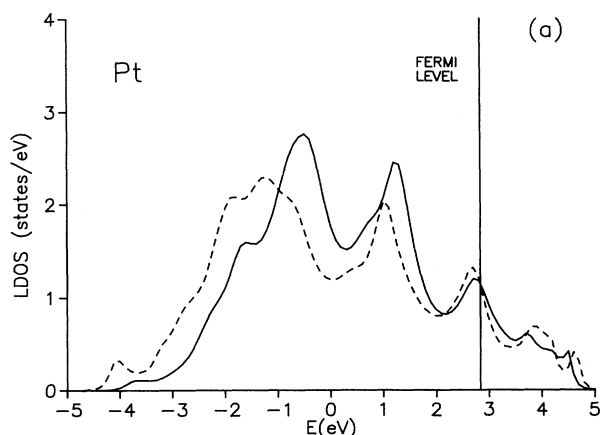


FIG. 4. LDOS for the Pt_3Ti alloy at the (111) surface (solid line) and in the bulk (dashed line). Results are shown for Pt atoms (a) and Ti atoms (b).

parts of energy bands. Enhancement of such peaks in the surface–non-SCF LDOS is explained by usual band-narrowing arguments.) For surface Ti atoms, the LDOS at the dip edge is not sensitive to the self-consistency and if any Ti-heteroatomic states are present they are not well split from the bulk states [Figs. 1(b) and 2(b)]. For NiTi and PtTi (011) surfaces [Fig. 3(a)] the two states in the M -LDOS region are somewhat less pronounced, whereas for Ti atoms we find an unconvincing indication of the heteroatomic state band near E_F [Fig. 3(b)].

At $M_3\text{Ti}$ (111) surfaces we find two surface features for all the three compounds in the M -derived bands, analogous to those of MTi alloys. They are, however, weaker now. As seen from Figs. 4(a) and 5(a), respectively, their existence depends on the surface SCF corrections. One resolves clearly Ti-heteroatomic states for both SCF and non-SCF calculations near E_F in the LDOS dip for

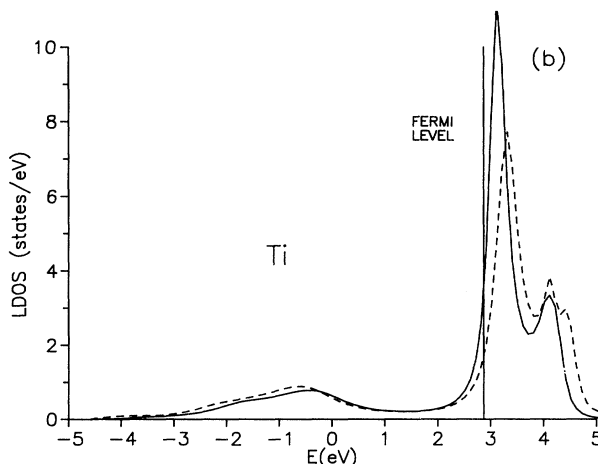
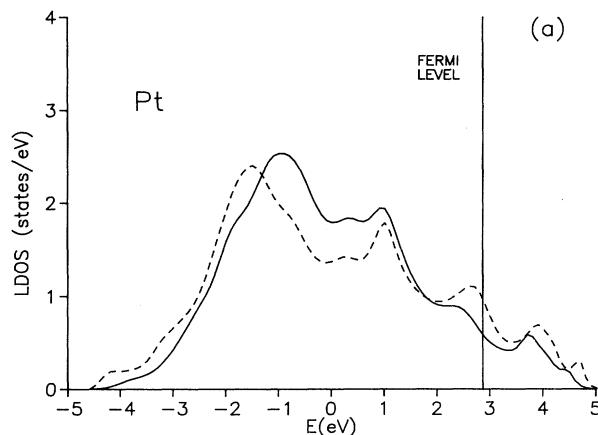


FIG. 5. The same as in Fig. 4. The surface–non-SCF results are shown.

$M=\text{Ni}$ and Pt [Figs. 4(b) and 5(b)]. For Pd_3Ti they are less marked.⁸

To summarize, we predict the existence of heteroatomic surface states at the nonpolar (111) surface of $M_3\text{Ti}$ alloys localized on Ti atoms at E_F . This feature, which may enhance the surface reactivity,¹ does not correlate with surface CLS's. For nonpolar MTi (011) faces a similar feature is very weak or is not present at all. For the surface M atoms we expect occupied surface states which should be accompanied by surface CLS's; these states are more important at MTi (011) faces. Although these filled bands probably do not influence the surface reactivity essentially, their experimental confirmation or refutation and the study of their behavior under different conditions could contribute to the understanding of the alloy surface properties.

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