

$=a^{-1}$  and the vertex function are very large for  $r_s \approx r_{s0}$ . Our approximation has the important consequence that  $B_{xc} = (a^2b - a_0^2b_0)/2$  remains finite and positive at  $r_s = r_{s0}$ , as expected on physical grounds.

<sup>25</sup>N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

<sup>26</sup>D. J. W. Geldart, M. Rasolt, J. H. Rose, and H. B. Shore, to be published.

<sup>27</sup>This has previously been shown to be important in the case of  $A_{xc}$  by B. Y. Tong, Phys. Rev. B 4, 1375 (1971).

<sup>28</sup>N. D. Lang and L. J. Sham, to be published.

## Observation of a Change in the Surface Electronic Structure of Pt(100) Induced by Reconstruction

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(Received 21 July 1975)

We investigated the clean surface of a Pt(100) single crystal in its stable ( $5 \times 20$ ) and metastable ( $1 \times 1$ ) configurations by ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, and low-energy electron diffraction. The photoelectron spectrum of the ( $1 \times 1$ ) surface for  $h\nu = 11.6$ – $40.8$  eV is characterized by a narrow peak 0.25 eV below the Fermi level; it is suggested that this peak is due to a maximum in the surface density of states associated with an electronic surface resonance or surface state on the ( $1 \times 1$ ) surface.

Certain crystallographic orientations of Pt<sup>1,2</sup> and Au<sup>3,4</sup> are characterized by surface reconstruction, i.e., the surface structure is not equivalent to that resulting from a termination of the bulk lattice. The question of whether this reconstruction of Au(100) and Pt(100) surfaces into the ( $5 \times 20$ ) structure, as evidenced by low-energy electron diffraction (LEED), is related to the presence of surface impurities was highly controversial for a number of years.<sup>5,6</sup> More recently, considerable evidence was brought forward on the basis of Auger electron spectroscopy (AES) and metal-overlayer studies,<sup>7,8</sup> which indicates that the reconstructed surfaces are very clean and most likely representative of the equilibrium surface of these metals. If this is the case, one would expect the clean, unreconstructed Pt(100)-( $1 \times 1$ ) surface, if it could be prepared, to exhibit a higher surface free energy and to be metastable. Furthermore, the difference in surface free energy and atom arrangement between the ( $1 \times 1$ ) and ( $5 \times 20$ ) surfaces should be accompanied by (and possibly due to) a difference in surface electronic structure.

In this Letter we report on the first successful preparation of the clean Pt(100)-( $1 \times 1$ ) surface which we studied using AES, LEED, and ultraviolet photoelectron spectroscopy (UPS). We find that this surface is indeed metastable and has a surface electronic structure (as determined by UPS) which is considerably different

from that of the ( $5 \times 20$ ) surface.

The experiments were performed on a well oriented, polished, Pt(100) single crystal (Marz grade, Materials Research Corporation) cleaned by *in situ* Ar-ion bombardment and high-temperature annealing up to 1100°C. The final surface was found to be free of impurities as judged from AES. The surface structure was characterized by a sharp ( $5 \times 20$ ) LEED pattern. This crystal was studied by UPS in the photon energy range 11.6–40.8 eV, with a dc resonance lamp using He, Ne, or Ar depending on which photon energy was desired. The angle of incidence of the photons was approximately 30° while the axis of the double-pass cylindrical-mirror analyzer (Physical Electronics Industries) made an angle of 15° with the sample normal. With this geometry, the measured electron energy distributions represent an average over polar angles of from approximately 27° to 52°. Other experimental details will be published elsewhere.<sup>9</sup>

As mentioned above, the equilibrium structure of a clean Pt(100) surface can be easily and reproducibly obtained by heating at elevated temperature, and it will always show a ( $5 \times 20$ ) LEED pattern.<sup>2,10</sup> On the other hand, the metastable ( $1 \times 1$ ) structure of a *clean* and well-annealed Pt(100) surface cannot be obtained by conventional techniques.

To obtain a clean ( $1 \times 1$ ) surface, one method we have used is a catalytic reaction between ad-

sorbed CO and  $O_2^+$  ions. The procedure was as follows: The clean Pt(100)-(5 $\times$ 20) surface was exposed to  $3 \times 10^{-6}$  Torr sec of CO. The adsorption of CO transforms the Pt (5 $\times$ 20) surface configuration to the desired (1 $\times$ 1) configuration. The CO was then removed at room temperature by reacting it with oxygen ions produced using a sputtering gun in an oxygen pressure of  $5 \times 10^{-7}$  Torr. The resultant CO<sub>2</sub> formed desorbs at room temperature leaving the sample surface free of carbon as determined by AES. A saturation coverage of CO could be removed by a total oxygen ion dose of approximately  $10^{-4}$  A sec/cm<sup>2</sup> (measured at the sample) using 250-V ions. After treatment the LEED pattern was a clear, *sharp* (1 $\times$ 1), indicating that minimal damage was done to the Pt surface. As a further test of this the (5 $\times$ 20) surface was given a similar oxygen treatment (no preadsorbed CO) with no observed change in the LEED pattern after treatment.

The clean (1 $\times$ 1) surface formed by this treatment is metastable; at temperatures above 125°C it transforms into the (5 $\times$ 20) structure which is then stable to higher temperatures or upon cooling. Based on this evidence the surface free energy of the 5 $\times$ 20 surface is clearly lower than that of the (1 $\times$ 1) surface.

UPS electron energy distributions were taken for both the clean (5 $\times$ 20) and (1 $\times$ 1) surfaces. Figure 1 shows the data for  $h\nu = 40.8$  eV. The

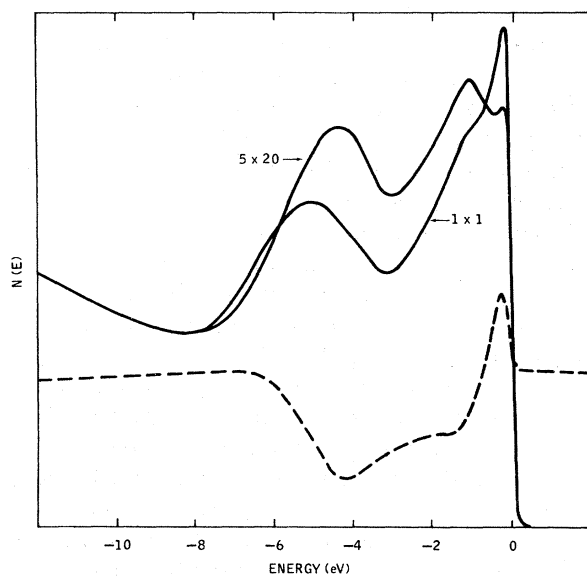


FIG. 1. UPS energy distribution curves for a clean Pt(100) surface,  $h\nu = 40.8$  eV. Dashed curve, difference spectrum between (1 $\times$ 1) and (5 $\times$ 20) structure.

energy distributions are plotted versus the electron's initial-state energy with the Fermi level taken as zero. The structure in the energy distributions is quite complex and will not be discussed in detail here.<sup>11,12</sup> The major difference between the (1 $\times$ 1) and (5 $\times$ 20) energy distributions appears 0.25 eV below the Fermi level; a narrow peak is observed for the (1 $\times$ 1) surface which is absent for the (5 $\times$ 20) surface. The difference  $\Delta N(E)$  between these curves is also shown; the presence of the peak for the (1 $\times$ 1) surface can be seen even more clearly in this curve.

Similar behavior was observed for the other photon energies at 16.8 and 21.2 eV.  $\Delta N(E)$  between the (1 $\times$ 1) and (5 $\times$ 20) surfaces at 40.8 and 21.2 eV is shown in Fig. 2. It is evident from the figure that the (1 $\times$ 1) surface is characterized by a strong peak near the Fermi level.

There are two plausible explanations for the large differences observed in the photoelectron spectra. First, the (5 $\times$ 20) surface does not have the same two-dimensional periodicity present for the (1 $\times$ 1) surface. Direct transition effects that would therefore be severely attenuated for the (5 $\times$ 20) surface. This explanation can probably be ruled out for the peak near the Fermi level, however, since it appears for all photon energies measured.

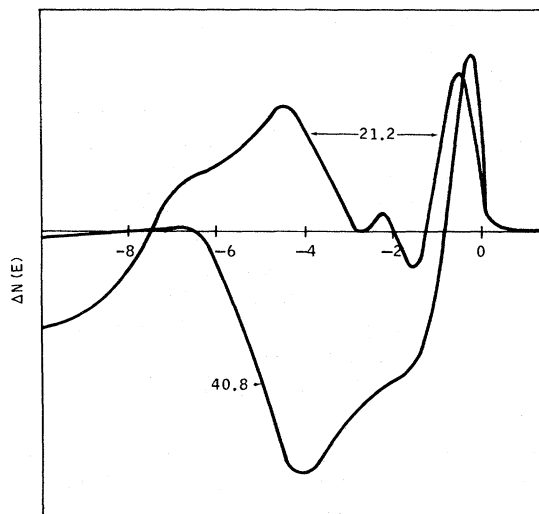


FIG. 2. UPS difference spectra between (1 $\times$ 1) and (5 $\times$ 20) surfaces plotted versus initial-state energy  $E$ ; photon energies as indicated.

Second, with a different atom arrangement in at least the uppermost layer, the surface density of states would be expected to be different for the two structures. Although the photoemission spectra can in no way be interpreted as mirroring the density of states, changes in the density of states will most certainly bring on changes in the photoemission spectra.

The effect of adsorption on the intensity of the peak near the Fermi level for the  $(1 \times 1)$  surface also gives support to arguments in favor of different density of states for the two surfaces. Figure 3 shows a set of UPS difference spectra for increasing exposure of the clean Pt(100)- $(1 \times 1)$  surface to CO at  $T = 50^\circ\text{C}$ . It can be seen that a significant decrease in surface-state emission is noted before any substantial UPS structure due to the adsorbate evolves. For about  $0.5 \times 10^{-6}$  Torr sec of CO exposure, a drop in intensity equal to the original peak height of the surface-resonance peak is observed.

There are some reasons to believe in fact that the peak observed near the Fermi level for the  $(1 \times 1)$  surface is due to an electronic surface

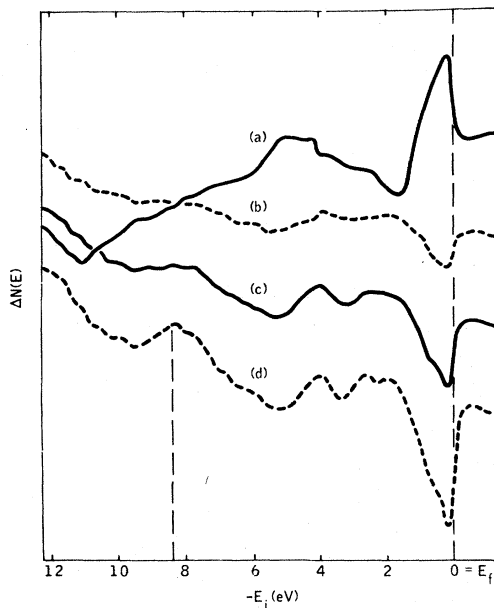


FIG. 3. UPS difference spectra for CO adsorption on the unreconstructed Pt(100)- $(1 \times 1)$  surface,  $h\nu = 21.1$  eV. (a)  $\Delta N(E)$  curve for clean  $(1 \times 1)$  structure minus clean  $(5 \times 20)$  structure; (b) after  $0.25 \times 10^{-6}$  Torr sec of CO; (c)  $0.5 \times 10^{-6}$  Torr sec of CO; (d)  $1 \times 10^{-6}$  Torr sec of CO. Note also the evolving emission peak at  $-8.4$  eV representative of molecular orbitals of CO (Ref. 9). Curves b-d with reference to clean  $(1 \times 1)$  structure.

resonance, which is associated with a relative gap in the Pt band structure along the  $\Gamma$ -X  $[100]$  direction. The gap is due to the spin-orbit interaction which is of order 1 eV for the  $5d$  transition metals.<sup>13</sup> Since there are no absolute gaps along the  $\Gamma$ -X direction, a surface state would be unlikely. This interpretation is consistent with recent theoretical calculations on the bcc metals of the  $5d$  transition series.<sup>14</sup> Relative gaps created by spin-orbit coupling give rise to peaks in the surface density of states, even though the eigenfunction for the state has some traveling-wave character. The existence of surface states or surface resonances has been extensively associated with unsaturated surface bonds. If this is the case for Pt(100)- $(1 \times 1)$  one would expect the chemisorption characteristics of the  $(1 \times 1)$  and  $(5 \times 20)$  surfaces to be different. Other results to be published elsewhere<sup>15</sup> on the chemisorption of  $\text{O}_2$  and  $\text{H}_2$  on Pt(100) support this conclusion. Basically neither  $\text{O}_2$  or  $\text{H}_2$  chemisorb at room temperature and low pressure on the Pt(100)- $(5 \times 20)$  surface whereas we have observed sticking coefficients for both these gases of between 0.1 and 1.0 on the clean  $(1 \times 1)$  surface.<sup>15,16</sup>

The results of the present investigation do not only provide evidence of a surface resonance for the unreconstructed Pt(100)- $(1 \times 1)$  surface, but they also strengthen the point of view that the  $(5 \times 20)$  surface structure is representative of the clean equilibrated Pt(100) surface. We observed that the temperature of the transformation  $(1 \times 1) \rightarrow (5 \times 20)$  was lower the cleaner the surface appeared by AES. Small concentrations of surface carbon stabilized the  $(1 \times 1)$  structure and raised the transformation temperature to  $> 400^\circ\text{C}$  in agreement with previous observations.<sup>10</sup> The stabilization of the  $(1 \times 1)$  surface by carbon also resulted in stabilization of the surface-state emission but the corresponding UPS difference spectrum showed an additional peak at  $-2.3$  eV which we attribute to carbon. On the basis of these findings it seems possible that very small amounts of carbon undetected by AES led to the stabilization of the  $(1 \times 1)$  surface at low temperature which enabled us to obtain UPS spectra of that particular structure. On the other hand, we conclude that the cleaner the Pt(100) surface the easier the  $(5 \times 20)$  structure will be formed (at lower temperatures), and that therefore the Pt(100)- $(5 \times 20)$  structure is a true equilibrium configuration of that surface.

Finally, we would like to comment on a pos-

sible connection between the existence of the surface resonance and the probability for reconstruction of metal surfaces. From an energetics point of view one might argue that the presence of the surface resonance near the Fermi level is concomitant with a high surface free energy which in turn would be a driving force for reconstruction. On the other hand, the existence of a surface resonance in this case presumably depends on spin-orbit splitting in the band structure of the metal.<sup>14</sup> If the width of the spin-orbit gap determines the strength of the surface state, it would also be a rough measure of the probability for reconstruction. It is interesting to note that the band structures of the noble metals<sup>13</sup> show a small spin-orbit splitting (of the order of 0.2 eV) for the 4*d* metals but a fairly large splitting for the 5*d* metals, namely about 1 eV. Of course, it is known<sup>17</sup> that the 4*d* metals Rh, Pd, and Ag do not reconstruct while the 5*d* metals Ir, Pt, and Au do reconstruct, at least the (100) and (110) orientations. It remains to be seen whether further experimental and theoretical work will be able to substantiate or disprove this hypothesis.

We would like to thank Traugott Fisher for many stimulating discussions.

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<sup>1</sup>S. Hagstrom, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Lett.* **15**, 491 (1965).

<sup>2</sup>H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.* **46**, 2539 (1967).

<sup>3</sup>D. G. Fedak and N. A. Gjostein, *Phys. Rev. Lett.* **16**, 171 (1966), and *Acta Metall.* **15**, 827 (1967).

<sup>4</sup>D. G. Fedak and N. A. Gjostein, *Surf. Sci.* **8**, 98 (1967).

<sup>5</sup>G. A. Somorjai, *Surf. Sci.* **8**, 98 (1967).

<sup>6</sup>J. T. Grant and T. W. Haas, *Surf. Sci.* **18**, 457 (1969).

<sup>7</sup>P. W. Palmberg, in *Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969).

<sup>8</sup>P. W. Palmberg and T. N. Rhodin, *J. Chem. Phys.* **49**, 134 (1968).

<sup>9</sup>H. P. Bonzel and T. E. Fischer, *Surf. Sci.* **51**, 213 (1975).

<sup>10</sup>G. A. Somorjai, *Catal. Rev.* **7**, 87 (1972).

<sup>11</sup>S. F. Lin, D. T. Pierce, and W. E. Spicer, *Phys. Rev. B* **4**, 326 (1971).

<sup>12</sup>N. V. Smith, G. K. Wertheim, S. Hüfner, and M. M. Traum, *Phys. Rev. B* **10**, 3197 (1974).

<sup>13</sup>O. K. Andersen, *Phys. Rev. B* **4**, 883 (1970).

<sup>14</sup>R. Feder and K. Sturm, *Phys. Rev. B* **12**, 537 (1975).

<sup>15</sup>C. R. Helms, H. P. Bonzel, and S. Kelemen, to be published.

<sup>16</sup>After the CO/O<sub>2</sub><sup>+</sup> treatment to produce the (1 × 1) surface, adsorbed oxygen was sometimes detected; it could be removed by the water synthesis reaction with H<sub>2</sub> and any residual adsorbed hydrogen removed by heating to 100°C. This effect will be discussed in more detail in Ref. 15.

<sup>17</sup>G. A. Somorjai, *Principles of Surface Chemistry* (Prentice Hall, Englewood Cliffs, N. J., 1972).

## Susceptibility of Interconfiguration-Fluctuation Compounds\*

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(Received 12 May 1975)

We present a simple model for the magnetic susceptibility of rare-earth compounds which exhibit interconfiguration fluctuations (ICF). It is shown that the temperature dependence of the magnetic susceptibility of several ICF Yb compounds can be fitted quantitatively, assuming an energy separation  $E_{ex}$  between the two configurations and an intrinsic lifetime  $\tau$  due to the 4*f*-shell-conduction-electron interaction. With the parameters  $E_{ex}$  and  $\tau$  obtained from such fits it is possible to predict the temperature dependence of the valence.

Recently, there has been a great deal of interest in metallic rare-earth compounds in which the rare-earth 4*f* shell apparently demagnetizes (i.e., neither orders magnetically nor shows a low-temperature Curie divergence). Through measurements of magnetic susceptibility, lattice

constant, resistivity, specific heat, Mössbauer isomer shift, x-ray absorption, and x-ray photoemission on rare-earth compounds such as SmB<sub>6</sub>, SmS, YbAl<sub>3</sub>, αCe, TmTe, and EuCu<sub>2</sub>Si<sub>2</sub>,<sup>1,6</sup> it has been established that nonmagnetic rare-earth ions can be described as fluctuating in time