

fast surface states at the same energy that is presented here.

In conclusion, we want to emphasize that the term "intrinsic" states, which is invoked here, does not imply presence of dangling bonds; it applies only to states of unsolvated surfaces. Even without any solvent interactions most semiconductors can and do minimize their surface energy by reconstructing the surface in a way that minimizes the number of the dangling bonds, but this reconstruction can still leave states in mid-gap that will be further influenced by chemisorption and solvation.

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## Probing the Local Density of States of Metal Surfaces by Deexcitation of Metastable Noble-Gas Atoms

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Resonance ionization followed by Auger neutralization is the mechanism for deexcitation of metastable noble-gas atoms (He, Ne, Ar) at metal surfaces which are either clean or covered with "small" atomic adsorbates and whose work function is  $\approx 4.5$  eV. The energy distributions of the emitted electrons reflect the self-convolution of the local density of states of the outermost atomic layer and thus provide a spectroscopic technique with extreme surface sensitivity as demonstrated with Pd(111) and Cu(110) surfaces.

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Experimental information on the electronic density of states of the outermost atomic layer of metals has so far been rather limited, since with photoelectron spectroscopy emission from the surface is usually overlaid by contributions from

the bulk.<sup>1</sup> Hagstrum's<sup>2</sup> ion-neutralization spectroscopy (INS)—where the electrons emitted from the solid upon impact of slow noble-gas ions are analyzed—probes only the surface layer,<sup>3</sup> but problems might arise from the relatively high

kinetic energy ( $\sim 10$  eV) of the ions involved.<sup>2,4</sup> This difficulty may be overcome by the use of electronically excited, metastable noble-gas atoms with thermal kinetic energy ( $< 0.1$  eV): The usefulness of this probe has already been recognized previously,<sup>5-9</sup> and the literature also contains reports on the deconvolution of recorded spectra<sup>6,8</sup> which were, however, at least partly questionable. In this Letter we describe what is believed to be the first reliable analysis of data obtained by this method and demonstrate what kind of information on the surface density of states (SDOS) can be obtained. This includes a comparison with existing theoretical calculations [for Pd(111)], as well as the identification of a band of surface states [with Cu(110)] and its modification by adsorption.

Collision of a metastable noble-gas atom with a solid surface leads with almost unit probability<sup>10</sup> to relaxation into the ground state and simultaneous electron emission from the solid. For the systems investigated in the present work deexcitation occurs according to the mechanism illustrated by Fig. 1(a): The electron in the excited state of the noble-gas atom tunnels into degenerate empty states of the solid (resonance ionization, RI). The remaining positive ion is then neutralized through an Auger process (Auger neutralization, AN) in an identical manner as with

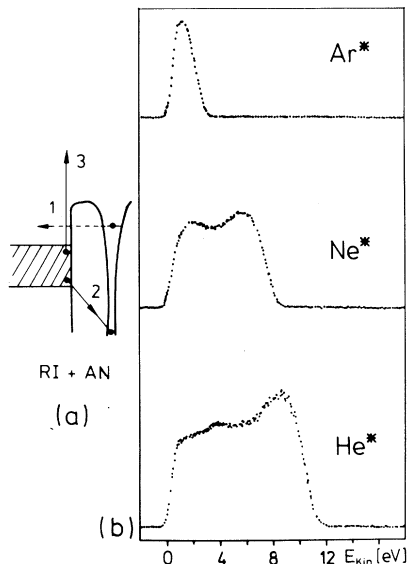


FIG. 1. (a) Deexcitation mechanism for metastable noble-gas atoms at metal surfaces: Resonance ionization (1) followed by Auger neutralization (2, 3). (b) Electron energy distributions from a clean Pd(111) surface excited by metastable He, Ne, and Ar atoms.

INS, which operates with positive ions from the beginning. Direct Auger deexcitation (AD) of the metastable atom, also called Penning ionization, is in principle possible as a competing mechanism and has been studied with several suitable systems,<sup>7,9,11-14</sup> but the transition rates of this process ( $\sim 10^{13}$  s<sup>-1</sup>)<sup>15</sup> are much smaller than those of resonance ionization ( $\sim 10^{15}$  s<sup>-1</sup>)<sup>16</sup> so that the RI and AN mechanism will always dominate as long as RI is possible. This is true for the systems treated in this work, namely metal surfaces (Pd, Cu) which were either clean or covered with "small" atomic adsorbates (e.g., O). The transition rate of the AN process is essentially determined by the overlap between occupied states of the solid and the hole state of the noble-gas ion in front of the surface. The origin of the emitted electrons is therefore restricted to the outermost atomic layer.<sup>3</sup>

According to Fig. 1(a) the AN process involves two electrons from the solid surface. Following Hagstrum<sup>2</sup> the energy distribution  $P(\zeta)$  of the emitted electrons is correlated with the electronic surface density of states (SDOS),  $N(\zeta)$ , through

$$P(\zeta) \sim \int_{-\zeta}^{\zeta} |H_{fi}|^2 N(\zeta - \epsilon) N(\zeta + \epsilon) d\epsilon. \quad (1)$$

$\zeta$  is the mean value of the binding energies (with respect to the Fermi level) of the two electrons involved and  $H_{fi}$  is the matrix element for the AN process. The kinetic energy of the corresponding emitted electron is given by

$$E_{\text{kin}} = E_{i, \text{eff}} - 2(\zeta + \varphi). \quad (2)$$

$E_{i, \text{eff}}$  is the effective ionization potential of the (ground-state) noble-gas atom in front of the surface which reflects the potential energy difference between the initial and final states at that distance at which the AN process occurs.  $\varphi$  is the work function of the solid. Through Eq. (2) the measured energy distribution  $P(E_{\text{kin}})$  can be transformed into  $P(\zeta)$ .

It is reasonable to assume that the matrix elements  $H_{fi}$  depend essentially only on the initial energies of the two electrons involved,<sup>2</sup> i.e.,

$$|H_{fi}|^2 = |H(\zeta - \epsilon)H(\zeta + \epsilon)|. \quad (3)$$

This transforms Eq. (1) into a self-convolution integral

$$P(\zeta) \sim \int_{-\zeta}^{\zeta} U(\zeta - \epsilon)U(\zeta + \epsilon) d\epsilon. \quad (4)$$

$U(\zeta)$  is the effective transition density, i.e., the SDOS weighted by the transition matrix element  $H(\zeta)$ . As a first approximation  $H(\zeta)$  will be pro-

portional to the overlap between the wave function of the hole state at the noble-gas ion and the involved wave function of the solid. As a consequence,  $U(\zeta)$  will reflect the SDOS from a "chemical" point of view, i.e., as "seen" by an atom approaching the surface.

Formalisms for the deconvolution of a self-convolution function of the type of Eq. (4) can be found in Refs. 17–19. In order to analyze the experimental spectra a computer program was developed based on the work by Garot and Boiziau.<sup>18</sup> The resulting data were tested according to criteria outlined by Hagstrum and Becker.<sup>17</sup> Further details will be described elsewhere.<sup>20</sup>

The experiments were performed by using metastable He, Ne, and Ar species which were produced by electron impact of atomic beams. The experimental arrangement is described in Ref. 14. Electron energy distributions could be recorded as a function both of angle of incidence of the metastable atoms and of angle of emission of the electrons. Although these parameters had some influence on the measured intensities, the energetic positions of the spectral structures were not affected: Since the AN process is governed by the overlap of localized wave functions, no  $k$ -conservation rules come into play as with ultraviolet photoelectron spectroscopy (UPS) (yielding information on the dispersion from angular-resolved experiments).

Figure 1(b) shows the electron energy distributions from a "clean" (i.e., without any adsorbates detectable by standard surface techniques) Pd(111) surface excited by He\*, Ne\*, and Ar\* atoms. The maximum kinetic energy is given for  $\zeta = 0$  [see Eq. (2)], i.e., if both electrons involved originate from the Fermi level. Since the ionization potentials decrease in the order He > Ne > Ar, the onset of the emission is shifted towards lower kinetic energies. This onset allows one in turn to determine the effective ionization potential  $E_{i, \text{eff}}$  which was found<sup>20</sup> to be typically about 2 eV lower than for the isolated atoms, in agreement with previous findings.<sup>5</sup> The broad maximum at high kinetic energies is caused by the self-convolution of the Pd  $d$ -band DOS. At low kinetic energies a background contribution from secondary electrons comes into play (as in UPS).

Deconvoluted spectra from Pd(111) are reproduced in Fig. 2 together with the local DOS for the outmost atomic layer as calculated by Louie<sup>21</sup> by using a self-consistent pseudopotential theory. Apart from a shaded peak at  $E_b = 6$  eV in the experimental distribution the structures of both

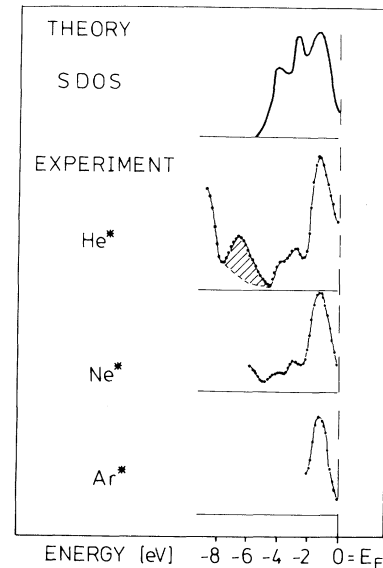


FIG. 2. Pd(111): Deconvoluted metastable spectra together with the theoretical SDOS (Ref. 21).

data are in excellent agreement with each other. The additional peak outside the  $d$ -band range originates from spurious amounts of impurities (far below the detection limit of Auger electron spectroscopy)<sup>20</sup> and demonstrates the extreme surface sensitivity of this technique. The intensity of the first peak below  $E_F$  is much more pronounced in the experimental than in the theoretical results which is attributed to matrix element effects: Since the wave function of metal levels higher in energy (i.e., closer to the Fermi level) will in general exhibit "tails" extending more into the vacuum, their overlap with the He hole state will also be stronger. This statement is confirmed by Louie's calculations.<sup>21</sup>

Figure 3(a) shows the Ne\* spectrum from a clean Cu(110) surface and the corresponding deconvoluted data. Angle-resolved UPS measurements with this system<sup>22</sup> identified a surface state within the  $s$ - $p$  band gap, i.e., energetically between  $E_F$  and the top of the  $d$  band. This surface state manifests itself in the deconvoluted spectrum as a peak below the Fermi level which has about the same intensity as the feature arising from the  $d$  band. It also clearly shows up in the direct experimental data [left-hand side of Fig. 3(a)] as a shoulder at high kinetic energies. Its energetic width is, however, considerably larger than with the cited UPS measurements for two reasons: The experimental resolution is about 0.3 eV in our case<sup>14</sup>; also, the metastable spectroscopy integrates over the whole energy

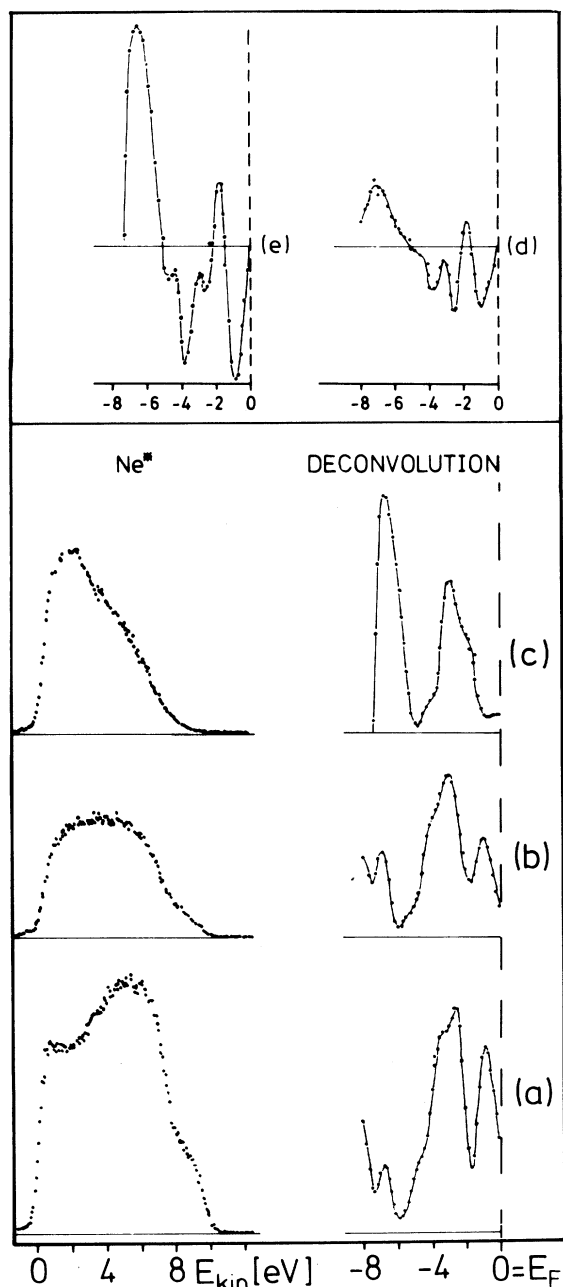


FIG. 3. Data for Cu(110). (a)–(c) Left-hand side, original Ne\* spectra; right-hand side, deconvoluted data. (a) Clean surface; (b) after 1 L O<sub>2</sub> exposure at 300 K; (c) after 10 L O<sub>2</sub> exposure. (d), (e) Difference spectra (b) – (a) and (c) – (a), respectively.

range of the dispersion. Self-consistent calculations for the SDOS have so far only been performed for the Cu(100) surface<sup>23</sup> and showed the formation of surface states which are heavily concentrated at the top edge of the *d* band which is at least in qualitative agreement with the

present findings.

A weak maximum at  $E_B = 7$  eV in Fig. 3(a) is again caused by the presence of spurious amounts of an atomic adsorbate. The drastic variations of the spectral features due to oxygen adsorption become evident from an inspection of Figs. 3(b) and 3(c), which represent the deconvoluted Ne\* spectra after 1- and 10-L [1 L (langmuir) =  $10^{-6}$  Torr s] exposures to O<sub>2</sub> at 300 K, respectively, as well as from the corresponding difference spectra of Figs. 3(d) and 3(e). The surface state below the Fermi level is strongly suppressed and disappears completely at 10-L O<sub>2</sub> exposure. On the other hand, a peak at  $E_B = 6.5$  eV grows continuously in intensity. This feature has also been observed with USP,<sup>24</sup> and is attributed to the bonding level arising from Cu-O(*2p*) coupling.<sup>25</sup> The difference spectra exhibit in addition a maximum at the top of the *d* band which is ascribed to the antibonding Cu-O(*2p*) level.<sup>25</sup> Oxygen adsorption under these conditions causes the formation of a  $2 \times 1$  LEED (low-energy electron-diffraction) pattern<sup>24</sup> which, according to recent ion-scattering<sup>26</sup> and He-diffraction<sup>27</sup> data, is associated with a reconstruction of the surface. The observation with the present technique of the pronounced peak from the bonding Cu-O level whose wave function is mainly O(*2p*) in character, however, clearly indicates that the oxygen atoms still have to protrude from the surface and cannot be "buried" between Cu atoms.

In conclusion, the examples discussed demonstrate the extreme surface sensitivity as well as the kind of information on the surface density of states of metal surfaces which can be achieved by proper analysis of the data obtained by metastable deexcitation spectroscopy.

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## 1/f Noise in Platinum Films and Ultrathin Platinum Wires: Evidence for a Common, Bulk Origin

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The 1/f noise of platinum films and ultrathin platinum wires has been found to scale inversely with the number of atoms in the sample,  $N$ , for  $N$  in the range  $10^7$  to  $10^{14}$ . This strongly reinforces the idea that the 1/f noise of continuous metal films is of bulk origin, and demonstrates that the dominant form of excess low-frequency noise in the very small structures investigated here is the bulk 1/f noise.

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Recently there has been much interest in the physics of very small structures. Progress in the fabrication of these structures has contributed greatly to the understanding of a wide variety of phenomena.<sup>1</sup> For example, the study of ultrathin wires ( $d \lesssim 500 \text{ \AA}$ , where  $d$  is the diameter) has provided new insight into the effects of impurities on electrical conduction in metals.<sup>2,3</sup> Another potentially fruitful area of research involving very small structures is the study of fluctuation processes. In most cases, the relative magnitude of a fluctuation is inversely proportional to the volume of the system,<sup>4</sup> so that one might expect that previously unobservable fluctuations could be extremely important in very small struc-

tures. One type of fluctuation whose effects may be readily measured is the electrical noise of a resistor. If the voltage across a resistor is sampled as a function of time, the noise-power spectral density,  $S_v(f)$ , may be obtained. When there is no current flow, we expect  $S_v = 4kTR$ , which is the well-known Johnson (Nyquist) noise.<sup>5</sup> When a direct current is passed through the resistor, however, noise in excess of the Johnson noise is commonly observed. The excess noise-power spectral density is often found to be proportional to  $1/f^\alpha$ , with  $\alpha \approx 1$ , and it is therefore referred to as "1/f noise." Although 1/f noise has been investigated extensively in recent years, its origin is not known.<sup>6,7</sup> Indeed, it is not yet