has been seen above the first-order transition in ErRh$_4$B$_4$.[8] In the same compound preliminary inelastic neutron scattering[9] has verified that $\chi_{BB}(q)$ peaks at a finite value of q as predicted here.

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Penning-Ionization Electron Spectroscopy of Chemisorbed CO

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Energy distributions of electrons ejected from clean and CO-covered Pd(111) surfaces by impact with metastable He* 2^1S (excitation energy $E^* = 20.6$ eV) and 2^3S ($E^* = 19.8$ eV) atoms were measured. The operation of the Penning mechanism, viz., He* $+A \rightarrow$ He $+A^+ +e^-$, is demonstrated for adsorbed CO whose valence orbitals could be identified. Thereby a new surface spectroscopic technique with extreme sensitivity to the outmost atomic layer is established.

Electron emission of metastable excited noble-gas atoms with clean and adsorbate-covered metal surfaces has been studied several times during recent years. The results, however, were often contradictory; the mechanism could not be established and almost no information on the surface properties could be obtained.[1-6] If, on the other hand, gaseous atoms or molecules are used as targets, electron ejection takes place through the Penning ionization (= Auger deexcitation) process, viz.,

$$\text{He}^* +A \rightarrow \text{He} +A^+ +e^-, \tag{1}$$

which has been well explored, both experimentally[7] and theoretically.[8] Similar conclusions were reached with condensed aromatics.[9,10] The kinetic energy of the emitted electrons, E_k, is then simply determined by the excitation energy of the metastable atom, E^* ($= 20.6$ eV in the case of 2^1S He), by the ionization energy of the target, E_i, and by the interaction potentials between the excited- and ground-state noble-gas atom with the target, $V^*(R)$ and $V(R)$, respectively. In the case of "hard core" interactions the variation with distance of the latter contributions becomes rather small so that E_i may be easily derived in a manner similar to ultraviolet photoelectron spectroscopy ($h\nu = 21.2$ eV for He I radiation). In

the following, electron energy distributions aris-
ing from collision of metastable He* atoms with
clean and CO-covered Pd(111) will be presented.
It will be demonstrated for the first time that the
Penning mechanism may also hold for adsorbed
phases on metal surfaces, contrary to all previ-
ous suggestions. Thereby we establish a new
surface spectroscopic technique which allows
identification of adsorbate valence levels and
which exhibits extreme sensitivity for the out -
most atomic layers.

The experimental apparatus consisted of two
parts: An ultrahigh-vacuum chamber (base pres-
sure $<2\times10^{-10}$ Torr) contained the sample mount-
ed on a manipulator and facilities for low-energy
electron diffraction, Auger electron spectros-
copy, ultraviolet photoelectron spectroscopy
(UPS), etc., as well as a rotable two-stage 127°
electron energy analyzer[11] which allows meas-
urements of electron energy distributions at
various angles of emission with respect to the
surface normal. Metastable excited He atoms
(2^1S, $E^* = 20.6$ eV, and 2^3S, $E^* = 19.8$ eV) were
produced by electron impact of a nozzle beam.[12]
The kinetic energy of the metastable atoms was
66 meV ($\cong 300$ K) and is thus below the limits of
energy resolution (~ 0.1 eV) and will be neglected
throughout the discussion. Highly excited He
atoms (Rydberg states) and ions were removed
from the beam by electric fields. The portion of
resonance photons (21.2 eV) was negligibly small
under the applied experimental conditions as
was demonstrated by time-of-flight measure-
ments. He* 2^1S atoms may be almost completely
(to less than 1%) quenched by resonance absorp-
tion from a He discharge lamp. It turned out
that the concentration of excited triplet (2^3S)
atoms was, under the applied conditions, always
less than 20% so that spectra recorded without
optical quenching correspond to practically pure
singlet excitation. The total flux of metastables
was about 10^8 sec^{-1} with a typical beam diameter
of about 3 mm at the sample surface.

Figure 1 shows electron energy distributions,
$N(E)$, from a clean surface excited by He I pho-
tons (UPS, curve a) as well as by singlet He*
(curve b). The lower energy scale refers in all
cases to the kinetic energy, E_k, of the emitted
electrons. The photoelectron spectrum exhibits
an abrupt decrease at high E_k which is caused by
the Fermi level E_F. If we take a value $\varphi = 5.0$ eV
for the work function, the origin of the scale for
E_k is fixed through $E_{k,\max} = h\nu - \varphi = 16.2$ eV. The
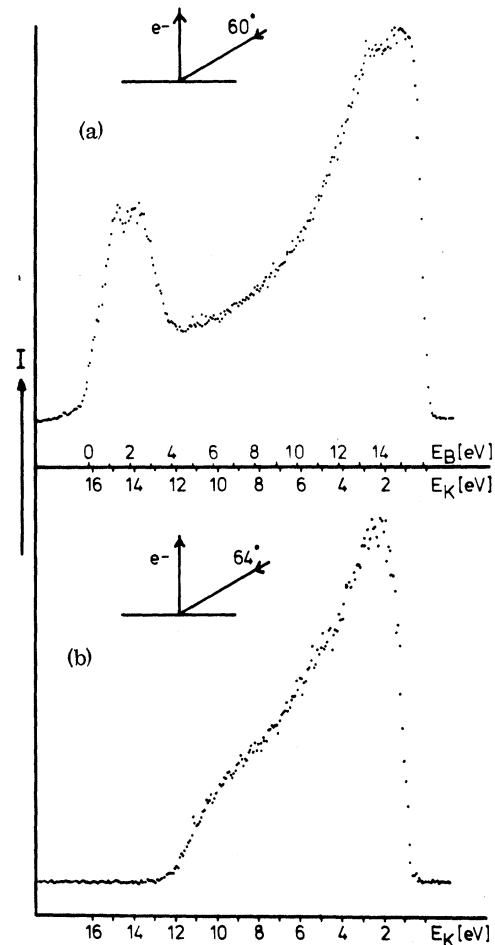same scale was applied for all other measure-

FIG. 1. Electron energy distributions from a clean
Pd(111) surface. (a) Photon excitation ($h\nu = 21.2$ eV);
(b) He* 2^1S excitation ($E^* = 20.6$ eV).

ments. The upper energy scale of Fig. 1(a) de-
notes correspondingly the electron binding ener-
gy with respect to E_F, i.e., $E_B = h\nu - \varphi - E_k$. The
pronounced structure between $E_B = 0$ and 4 eV
arises from the metallic d states.

The 2^1S-He*-excited spectrum from the clean
surface (curve b) exhibits—apart from the struc-
ture arising at the lowest kinetic energies—a
broad maximum centered at about $E_k = 9$ eV and
a cutoff at $E_{k,\max} \approx 12$ eV.

Electron energy distributions from a CO-cov-
ered Pd(111) surface (coverage $\theta = 0.5$) are re-
produced in Fig. 2. The photoelectron spectrum
(curve a) exhibits (compared with the situation
observed with the clean surface) additional max-
ima at $E_B = 8.2$ eV and ~ 11 eV. The latter fea-
ture becomes more clearly discernible with
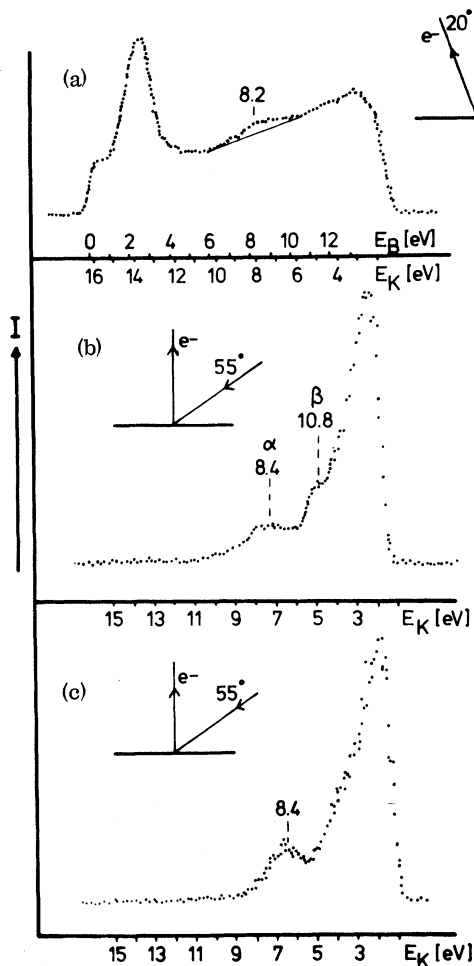He II excitation ($h\nu = 40.8$ eV).[13] The maximum

FIG. 2. Electron energy distributions from a CO-covered Pd(111) surface. (a) Photon excitation ($h\nu = 21.2$ eV), (b) He* 2^1S excitation ($E^* = 20.6$ eV), and (c) He* 2^3S excitation ($E^* = 19.8$ eV).

at the lower binding energy is identified with emission from CO-derived $5\sigma + 1\pi$ states; that at 11 eV arises from the CO 4σ level.[14]

The spectrum obtained by singlet He* (2^1S) excitation (curve b) exhibits a maximum at $E_k = 7.3$ eV (α) and a shoulder at $E_k = 4.8$ eV (β), the latter being on the slope of the pronounced increase of emission at very low kinetic energies. Note that there is no emission for $E_k \gtrsim 9$ eV.

Experiments performed with triplet He* (2^3S) atoms (curve c) revealed quite similar spectra, except that both structures occurred at kinetic energies about 0.8 eV lower than with singlet He* (2^1S) excitation. This value is just the difference in the excitation energies of the two species (20.6 – 19.8 eV). This effect clearly rules out any mechanism in which as a first step the ex-
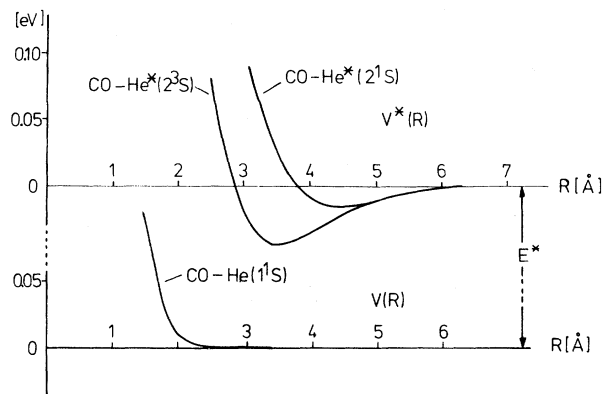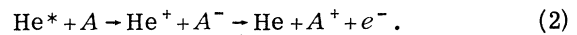

FIG. 3. Calculated potentials $V^*(R)$ and $V(R)$ for the configuration C-O$\cdots$He. R is the distance between the O and He nuclei.

cited electron is transferred to the metal (resonance ionization) and where the ion formed is subsequently neutralized and an electron is emitted via an Auger process, viz.,

$$He^* + A \rightarrow He^+ + A^- \rightarrow He + A^+ + e^-. \qquad (2)$$

Such a mechanism is operating in ion-neutralization spectroscopy (INS) as developed by Hagstrum,[15] where electron emission caused by collision of He$^+$ ions is studied, and was suggested also to hold for impact with neutral metastable He atoms.[1,7,16] Apart from the fact that the electron energy distributions measured with INS on a CO-covered surface look quite different from the present ones,[17] there would be no possibility to explain the observed difference by 0.8 eV between He* 2^1S and He* 2^3S excitation with an INS mechanism. The mechanism of Penning ionization as described by Eq. (1) may be illustrated by Fig. 3 which shows the variation of the potential with distance from the surface for the excited [$V^*(R)$] and the ground-state [$V(R)$] He atom as calculated with a local-spin-density functional formalism.[18] $V^*(\infty) - V(\infty) = E^*$ is the excitation energy of the noble-gas atoms. For a transition (either by exchange or nonexchange mechanism[9]) at a certain distance R according to Eq. (1) the kinetic energy of the emitted electron will be determined by

$$E_k(R) = V^*(R) - V(R) - E_i. \qquad (3)$$

Measurements with gaseous CO (Ref. 19) revealed the existence of only rather flat minima for $V(R)$ and $V^*(R)$, and a similar behavior is also suggested by the shown results of the calculations for adsorbed CO, so that $V^*(R) - V(R)$

$\approx V^*(\infty) - V(\infty) = E^*$ and accordingly

$$E_k = E^* - E_i. \tag{4}$$

If the ionization energy E_i is not referred to the vacuum level but instead to the Fermi level, namely, $E_B = E_i - \varphi$, we obtain (with $\varphi = 5.0$ eV as with the UPS experiments) $E_B \approx E^* - \varphi - E_k$ = 15.6 eV $- E_k$ for He* 2^1S and $E_B = 14.8$ eV $- E_k$ for He* 2^3S. Conversion of the energy scales in Fig. 2 in this way yields for the CO-derived maxima $E_B = 8.4$ and 10.8 eV, which are almost exactly the same numbers as derived with UPS. These maxima are therefore analogously identified with levels derived from the CO $1\pi + 5\sigma$ and 4σ levels, respectively.

The fact that with a CO-covered surface only adsorbate-derived levels and no features arising from metallic d states are observed (there is no emission between $E_B = 0$ and 6 eV) indicates that the metal is completely "shielded" by the adsorbate and that this technique probes only those states whose wave functions overlap sufficiently with the He* orbitals during the collision. Competition of the INS process with Penning ionization is in the present case obviously strongly suppressed since the tunneling probability of the excited electron through the adsorbate layer into an empty metallic state above the Fermi level is small. It cannot be ruled out, however, that the increase of the electron emission near threshold arises from electrons originating from the INS mechanism rather than from "true" secondaries.

The situation is different with the clean surface where the probability for resonance ionization of the impinging He* atom followed by Auger neutralization (equal to INS) is certainly much higher and might eventually dominate over the Penning ionization mechanism. The observed range of kinetic energies of the emitted electrons could indeed be well described by the operator of the INS mechanism if an effective neutralization energy of He$^+$ about 2 eV less than the value for the free ion is assumed.[17] Experiments with singlet and triplet He* atoms were not decisive in this case since the energy distributions exhibit a smooth tail at high kinetic energies which render the determination of $E_{k,\text{max}}$ uncertain. However, also a possible mechanism in terms of Penning ionization may be offered. Since an excited He* atom is chemically quite similar to a Li atom (which may be strongly chemisorbed at a clean transition-metal surface) it is to be expected that the potential $V^*(R)$ is no longer to the hard-core type but exhibits a pronounced minimum. If the

incoming He* atom is trapped in this potential and undergoes an electronic transition to $V(R)$ from the minimum of $V^*(R)$ the released energy will be considerably smaller than E^* and according to Eq. (3) also lower values for E_k will result. If the onset of emission in Fig. 1(b) at $E_{k,\text{max}}$ = 11.8 eV is tentatively identified with the Fermi level of the metal, the depth of the potential minimum of $V^*(R)$ is found by simple arguments to be 3.8 eV, which appears to be of the right order of magnitude if compared with the adsorption energy of 2.7 eV for Li on W.[20] Additional experiments will certainly be necessary in order to clarify this problem.

Preliminary measurements with a CO-covered surface at varying angles of electron emission revealed pronounced effects on the relative intensities of the maxima induced by the adsorbate levels. It is suggested that information on the symmetries and spatial orientations of the ionized orbitals may be obtained from systematic experiments together with a proper theoretical analysis.

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Nonequilibrium Superconducting States with Two Coexisting Energy Gaps

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The effect of tunnel currents in superconducting junctions on the energy gap is calculated. For certain parameters, two different gaps can exist. The stability of these solutions is investigated and at a certain voltage a "first-order transition" is found. This result explains the experimentally observed inhomogeneous states in superconducting tunnel junctions.

Recent experiments on superconducting tunnel junctions[1,2] suggest that for certain injection currents and voltages a superconductor sustains simultaneously two different values of the energy gap. Existing phenomenological models[3] predict that above a critical density of the excitations n_c, the superconductor has an intrinsic instability with respect to the formation of a spatially inhomogeneous state. This is not in agreement with the experimental results of Gray and Willemsen.[2] These authors interpreted the effect by existing inhomogeneities in the probes, with a lower gap value, which grow with increasing total current.

In this Letter we describe microscopically a superconducting tunnel junction consisting of an injector and a probe and find that two stable values of the energy gap can exist in the probe. In accord with the experiments, at a certain voltage a first-order phase transition takes place where the part of the probe with the lower gap and larger injection current density grows while the part with the larger gap and lower injection current density decreases. The relative size of the two regions is controlled by the total injection current. This is analogous to a liquid-gas transition at a certain pressure where the relative volumes are controlled by the total volume. Existing spatial inhomogenities will serve as nucleation centers for the low-gap region. To this extent, our result is similar to the model of Ref. 2. However, we find the existence of the two gaps to be an intrinsic property of the superconductor and the size of the low-gap regions grows continuously from zero to the size of the probe. Furthermore, our approach describes the gap enhancement by quasiparticle extraction, investigated in the experiments by Chi and Clarke.[4] We will present a detailed analysis in two limits, near T_c and near $T = 0$. Qualitatively, the same results can be obtained for any intermediate temperature.

We assume that the injector is thick and, in contrast to the probe, is not appreciably perturbed by the tunneling processes, and also that the phonons remain in equilibrium. The modification of the density of excitations in the probe affects Δ, the magnitude of the gap in the probe.