Field-Ion Spectroscopy of Electronic States at Clean and Adsorbate-Covered Tungsten Surfaces

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Measurements are reported of the kinetic energy distributions of field-ionized noble gases on both clean and nitrogen-adsorbate–covered surfaces of tungsten. The structure observed is attributed to the energy distribution of unoccupied electronic states at the metal surface. Correspondences are found with recent calculations of one-dimensional densities of states. A nitrogen-adsorption peak is observed at 0.6 eV above the Fermi energy.

The field-ion microscope, developed by Müller,[1] is perhaps the most direct method of examining the atomic structure of metal surfaces. In this Letter, we concentrate on one of the less explored aspects of field ionization, namely the ion energy distributions. We present measurements of the field-ion energy distributions (FIED's) on both clean and adsorbate-covered surfaces of tungsten, and we argue that they reflect the distribution of electronic states in the unoccupied energy region from 0 to about 4 eV above the Fermi level, E_F. This energy range is inaccessible in photoemission spectroscopy[2] and conventional field-emission spectroscopy.[3] Field-ion spectroscopy promises, therefore, to be a powerful complementary technique in the investigation of the electronic structure of surfaces.

The field-ionization process is illustrated schematically in the potential energy diagram of Fig. 1. A neutral atom (He or Ne in the work presented here) approaches a metal surface which is held at high positive potential. An electron may then tunnel from the atom into the metal under the influence of both the external field and the surface force. Depending on the distance from the metal, the energy at which the electron enters can vary in the range from 0 to a few electron volts above E_F. The energy distribution of such electrons, and therefore of the emitted ions, should reflect the density of unoccupied states.

The field-ionization process can be regarded, in some sense, as the inverse of the field-emission process. In the latter, electrons tunnel out of the metal, and their energy distribution reflects the occupied density of states.[4] Field ionization is a more complicated process than field emission because of the presence of the ionizing atoms which provide a three-dimensional potential barrier for the tunneling.[5,6] However, certain features of the theory of field emission are expected to survive. In particular, the tunneling

in field ionization has a preferred direction parallel to the field, and thus one expects some tendency for the FIED's to replicate the one-dimensional density of states for the unoccupied levels, just as field emission spectra do for the occupied levels.[4] Fortunately, Christensen and Feuerbacher[7] have recently calculated the one-dimensional density of states for several symmetry directions in W, and our experimental spectra will be compared with their results below. Of course, the ionization rate in a given energy range will be influenced not only by the density-of-states factor, but also by the tunneling transition matrix element. Here we will consider only the density-of-states effects.

The experimental apparatus will be described in detail elsewhere.[8] Very briefly, the instrument consists of a field-ion microscope with a 0.9-mm probe hole on a 75-mm-diam fluorescent
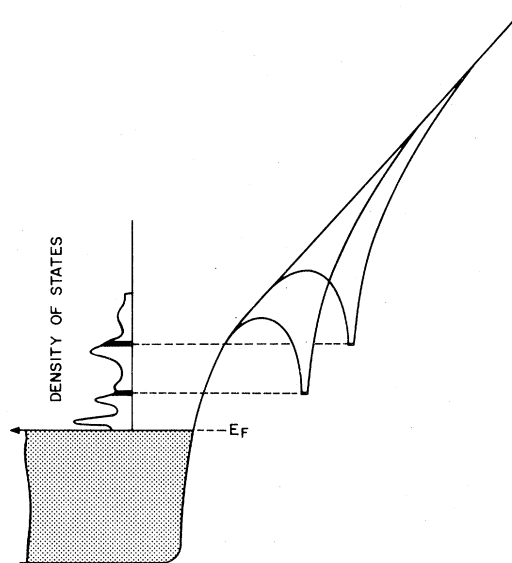

FIG. 1. Schematic potential-energy profile illustrating the field ionization of an atom in the vicinity of a metal surface.

screen, a retarding lens, a double-grid retarding energy analyzer, and a Channeltron ion detector. The overall energy resolution is estimated to be less than 0.2 eV. The sample tip was 50 mm from the screen and could be cooled to liquid hydrogen temperature. Base pressures were in the low 10^{-10}-Torr range.

We present first the results on clean W. The open circles in Fig. 2 represent the measured FIED on a clean (100) face of W. The Fermi level has been placed at the main peak, a position consistent with a detailed analysis of the Jason effect. On the decaying high-energy side of this main peak, three additional humps are observed at 1.3, 2.0, and 2.7 eV above E_F. The one-dimensional density of states for the $\langle 100 \rangle$ direction in W calculated by Christensen and Feuerbacher,[7] shown as a full curve in Fig. 2, has a peak at 2.0 eV above E_F which coincides closely with one of the observed peaks. In addition to this bulk density of states (BDOS), Christensen and Feuerbacher have calculated also a one-dimensional "surface density of states (SDOS)" which is shown as the dashed curve in Fig. 2. The SDOS is calculated from a bulk band structure in which the width of the d bands has been squeezed in order to simulate the effects of the reduced number of neighbors for surface atoms.[9] The one-dimensional SDOS has peaks at 1.25 and 2.7 eV, which also coincide quite closely in energy with two of the observed structures. We are therefore unable to say, on the basis of these measurements, which of the one-dimensional densities of states is the more appropriate.

Results obtained for the (110) face of W for two different tip voltages are shown in Fig. 3. The FIED exhibits small and closely spaced humps at 0.2, 0.6, 1.1, 1.5, 2.0, and 2.4 eV above E_F. This is also in agreement with the calculations of Christensen and Feuerbacher. The one-dimensional BDOS has peaks at 1.45, 2.0, and 2.8 eV above E_F, and the SDOS has peaks at 1.25, 1.6, and 2.3 eV. The humps observed experimentally at 0.2 and 0.6 eV, however, do not correspond to anything in either the BDOS or the SDOS. These structures may arise through either (i) enhanced tunneling transition probabilities, or (ii) the existence of unoccupied surface states, similar in nature to the occupied surface states observed in field emission[10] and photoemission,[11] or (iii) inapplicability of a strict one-dimensional approximation. In connection with possibility (iii) and the three-dimensional nature of the tunneling barrier, it is reasonable to suppose that we are actually sampling the Brillouin zone along a range of directions centered about the principal direction. It could be that the bulk band structure accounts for most of our observations and that the SDOS considerations and other mechanisms are largely unnecessary. Clearly, there is a need for some theoretical work to resolve these points.

The connection between the field-ionization rate and the unoccupied density of states may be responsible for some of the beautiful regional
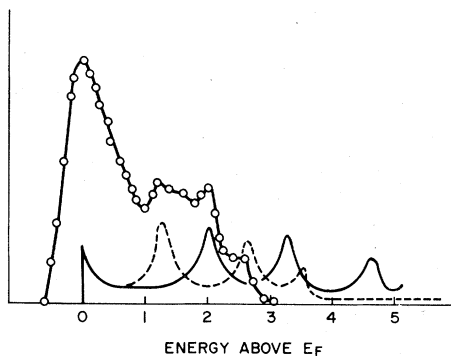
FIG. 2. The measured FIED of He on the (100) face of W, indicated by the open circles, is compared with the calculations of Christensen and Feuerbacher (Ref. 7). Solid and dashed curves represent the one-dimensioned BDOS and SDOS, respectively. The FIED was taken at a tip voltage of 2.3 kV [field-evaporation voltage (FEV) = 3.62 kV] and a tip temperature of 21°K.
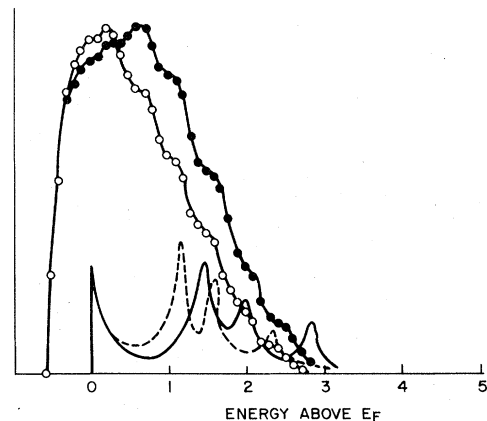
FIG. 3. Two measured FIED's of Ne on a (110) face of W are compared with the calculations of Christensen and Feuerbacher. Solid and dashed curves represent the one-dimensional BDOS and SDOS, respectively. The curve connecting the open circles was taken at a tip voltage of 3.1 kV (FEV = 3.4 kV), and curve connecting full circles was taken at 4.2 kV (FEV = 4.35 kV). Tip temperature is 78°K for both cases.

brightness patterns observed in field-ion micro-
graphs of various metals using samples of large
tip diameter. Perhaps the most clear-cut exam-
ple is the relative brightness of the $\{111\}$ regions
in the field-ion micrographs of Pt and Ir. (See
Figs. VI.8 and VI.9 of Ref. 1.) In Pt, the band
structure of Andersen[12] indicates that along ΓL
there exists a band gap extending from about 0.3
eV to about 5.9 eV above E_F. This sparsity of
states in the energy range a few eV above E_F is
consistent with the darkness of the $\{111\}$ regions.
In Ir, which has one less electron per atom than
Pt, the Fermi level falls lower with respect to
the top of the d bands.[11] There is therefore a
high concentration of d-like states just above E_F,
consistent with the relative brightness of the
$\{111\}$ regions in Ir.

The FIED obtained after N_2 adsorption at 300°K
is indicated in Fig. 4. Peaks characteristic of
clean W(100) are observed at the same energies
as in Fig. 1. In addition, the spectrum exhibits
a distinctive new peak at 0.6 eV above E_F, which
we attribute to an unoccupied electronic level of
either (a) a tungsten-nitrogen surface complex,
or (b) a new state which comes about through the
rearrangement of surface tungsten atoms on
field desorption of nitrogen. Disappearance of
this new peak occurs only at voltages large enough
to produce field evaporation of tungsten atoms,
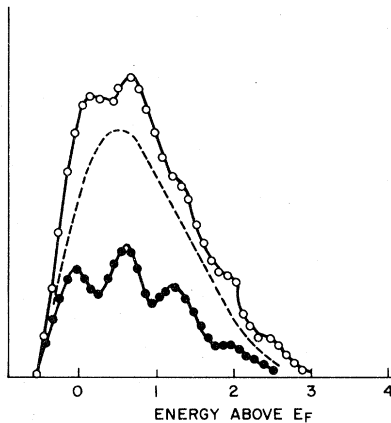making it difficult to distinguish between (a) and
(b).[13]

The FIED obtained after adsorption at 21°K is
shown in Fig. 4. Structures are observed at the
same energies as in the 300°K adsorption spec-
trum, but are somewhat weaker and are riding
on a featureless background which we have re-
presented by the dashed curve in Fig. 4. On in-
creasing the voltage to 3.1 kV (82% of the field-
evaporation voltage), there is a drop in the total
field-ionization rate, indicating the removal of
weakly bound nitrogen by field desorption. The
general appearance of the FIED after this field
desorption resembles closely that obtained in the
nitrogen-adsorption experiment at 300°K. On fur-
ther increasing the voltage to 3.5 kV, the spec-
trum becomes very close to that of clean W(100)
as shown in Fig. 1.

In conclusion, we have demonstrated the capa-
bilities of a new experimental technique, field-
ion spectroscopy, for the study of the unoccupied
electronic states at both clean and adsorbate-cov-
ered metal surfaces.

FIG. 4. Measured FIED's of He taken after the ad-
sorption of nitrogen on the (100) face of W. The curve
connecting the filled circles was taken after N_2 adsorp-
tion at 300°K; the tip voltage was 2.3 kV (FEV = 3.68
kV). The curve connecting the open circles was taken
after N_2 adsorption at 21°K; the tip voltage was 2.16
kV (FEV = 3.62 kV). Relative intensities are approxi-
mate.

ENERGY ABOVE E_F

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Lattice Dynamics of a Single Crystal of PdD$_{0.63}$†

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The frequency–wave-vector dispersion relations of a single crystal of PdD$_{0.63}$ have been measured by coherent neutron inelastic scattering at 78, 150, 220, and 295 K. The acoustic modes are considerably lower in frequency than the corresponding modes for pure Pd, in accord with the observed lattice expansion. The optic modes, in which D motions predominate, show considerable dispersion. In particular, the shape of the [100] LO branch shows conclusively that second–like-neighbor D-D interactions are comparable to the first–like-neighbor D-D interactions.

The physical properties of metal hydrides have been studied extensively for many years.[1] Recently there have been even more vigorous efforts in the investigation of the microscopic properties of hydrides, in part as a result of the increasing importance of metal-hydrogen systems in technological applications.[2] This has lead to renewed emphasis on the electronic structure and interatomic forces which underlie the properties of these multiphase solids, and for which the existing experimental information is often contradictory.[2] To date there have been no experimental results which could give direct information on the metal-hydrogen and hydrogen-hydrogen forces in these materials. In this Letter we present the first detailed measurements of the phonon dispersion relation in a metallic hydride—PdD$_{0.63}$. The only previous data on the dynamics of β-phase palladium hydride were derived from incoherent neutron scattering[3,4] on polycrystalline samples. The present results, derived from coherent neutron scattering on a

single-crystal sample, show in detail that the picture of the dynamics derived from the earlier measurements is in error. In particular, we find large dispersion in the longitudinal optic modes (which are dominated by deuterium motions)—a result in direct contradiction with the theoretical results recently obtained by Hertel[5] in an attempt to correlate the lattice dynamics and the superconducting properties[6,7] of nearly stoichiometric PdD and PdH. In addition we find that the frequencies of the acoustic modes are considerably changed from those in palladium, again in contradiction to existing theoretical predictions.[5] The present sample certainly has a superconducting temperature less than 1 K, so that pronounced phonon anomalies like those observed in the transition-metal carbide[8-10] are neither expected nor observed. However, the present results do show conclusively that strong interactions between deuterium atoms extend to more than nearest neighbors and that the lattice dynamics of palladium hydride can only be ex-