Fig. 3. Statistical observations of this type, based on a sample of 300 or so measurements, cannot detect interactions[6] for which $|W(x)| \approx kT/2$. Within this limit, there is no indication of any interaction between members of a self-adsorbed pair of tungsten atoms at distances $R > 7$ Å.

Long-range forces might be expected from two sources: dipole-dipole effects between atoms polarized at the surface, and indirect, or band-structure-mediated, interactions. Tungsten atoms adsorbed on the (110) plane of tungsten, for example, have been found to carry a dipole on the order of 1 D.[8] Even for such highly polarized atoms, however, the direct electrostatic interactions at room temperature are already comparable to kT beyond 3 Å. Indirect interactions on tungsten, estimated by Einstein and Schrieffer,[9] decay rapidly with distance, and are on the order of kT at distances larger than 6 Å. For the distances covered, our direct measurements are therefore in agreement with the present, limited, understanding of forces at a metal surface.

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d-Band Contributions to the Energy Distribution of Field-Emitted Electrons from Platinum-Group Metals*

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Experimental field-emission spectra for the principal planes of the fcc transition-group metals (iridium, rhodium, palladium, and platinum) exhibit significant systematic agreement with relativistic augmented–plane-wave band calculations by Andersen. Surface band-edge contraction as well as effects of chemisorbed hydrogen and nitrogen are discussed.

The potential applicability of field-emission energy-distribution (FEED) spectra as a tool for detailed band-structure studies has been critically reviewed by Gadzuk and Plummer.[1] The crystallographic and energy sensitivities of the FEED spectra in the direction normal to the surface provide an effective probe of the electron structure within about 2 eV of the Fermi energy. Comparisons between experimental FEED spectra and calculated bulk band structures have been limited heretofore by uncertainties in the interpretation of the spectra and reliability of the calculations. It follows from the tight-binding model for the *d*-band wave function that the *d*-band contributions can be smaller than the *s*-band contributions by as much as a factor of 100.[1-5] A FEED study of the metals (Ir, Rh, Pd, Pt) from Group VIII provides an excellent scheme to investigate the *d*-band contribution to the tunneling current. We have new experimental results for many of the principal faces of these metals field evaporated at 78°K, showing systematic similarities between experimental FEED spectra[6] and calculated band structures.[7] The discussion here is limited to the $\langle 111 \rangle$ crystal direction of surfaces of Ir, Rh, Pd, and Pt. The data were taken on a new design high-resolution energy analyzer chosen to operate at 50 meV, to be discussed elsewhere.[6]

Previous measured energy-distribution studies have been reported for copper[8] and for tungsten and molybdenum.[9-12] Field-emission calculations have been made by Gadzuk,[3] by Politzer and Cutler,[4] and by Duke and Fauchier.[5] Gadzuk and Plummer[1] conclude that the dominant contribution of tunneling from the s-p bands explains the gross features of the field-emission phenomena.

Field electron emission has recently been shown to probe the local one-dimensional density of states at the metallic surface.[13,14] The field-emission current density per unit energy is approximately proportional to the product of the barrier-penetration probability $D(\epsilon_i)$; the spatial density of the ith single-electron state at the classical turning point, $(\Psi_i{}^*\Psi_i)_{\text{tp}}$; and the Fermi function $f(\epsilon)$ summed over all states at energy ϵ:

$$J(\epsilon) \approx Cf(\epsilon)\textstyle\sum_i D(\epsilon_i)(\Psi_i{}^*\Psi_i)_{\text{tp}}\,\delta(\epsilon-\epsilon_i),$$

where C is a slowly varying function of ϵ. Because of the strong, exponential dependence of $D(\epsilon_i)$ upon the component of momentum normal to the metallic surface, the local surface density of states should readily be extractable from field-emission–current spectra.[13]

Relativistic augmented–plane-wave band-structure calculations for rhodium, palladium, iridium, and platinum by Anderson[7] predict that the location of the strongly hybridized d bands is in the vicinity of the Fermi level. In particular, for Ir(111) and Pt(100), the tops of some of the d bands ($L_6{}^-$ and $X_7{}^+$, respectively) lie below the Fermi level, convenient for study by electron-tunneling measurements. The contributions from the overlapping bands should be separable near the band edges. A detailed inspection of the calculated band structures[7] for all four transition metals (Rh, Pd, Ir, Pt) indicates significant correlation of the electron band structure with specific features of the measured FEED spectra.[6]

In Fig. 1 the field-emission probe hole current is plotted as a function of electron energy in the ⟨111⟩ direction. The decomposition of Fig. 1(a) (indicated by the dashed curve) is made on the simple premise that the spectrum can be resolved into contributions among the overlapping bands. Specifically, the fourth band is assumed to have an s-p–like contribution for which, according to standard theory,[1] $\ln J(\epsilon)$ varies linearly with ϵ. Thus, fitting a straight line to the low-energy portion of the curve and extending a smooth (best judgment) curve down from the high-energy portion, we are able to separate the contribution of the fourth (Λ_4) band from the composite contributions of the fifth and sixth bands to the total energy spectrum.

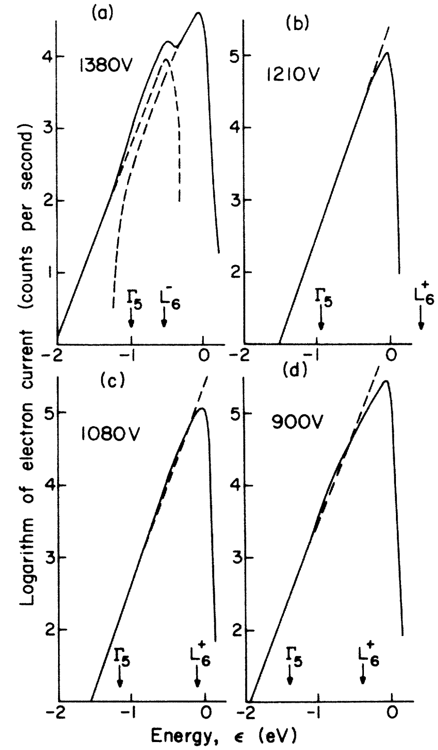

FIG. 1. Field-emission energy distributions for the clean (111) planes of (a) iridium, (b) rhodium, (c) palladium, and (d) platinum, at 78°K. The natural logarithm of the count rate is plotted against normalized energy ϵ, in electron volts ($\epsilon = 0$ is the approximate Fermi level). Data were taken in 25-meV steps at 5 sec per point. For Ir(111), decomposition is indicated by the dashed curves. The arrows indicate the calculated band-edge locations.

The corresponding band structures[7] are shown in Fig. 2. A broad, reproducible shoulder develops on the exponential portion of the spectra below the Fermi level ($\epsilon = 0$) for Ir(111). A similar hump reported[9,10] for W(100) and Mo(100) is interpreted in terms of intrinsic surface states based on combined FEED[1,11,12] and photoemission results.[15] Since the fourth (Λ_4) band in Fig. 2(a) is somewhat s-p–like, its features are compared to the standard FEED formulation.[9] First, the extrapolated location of the fourth-band maximum in Fig. 1(a) appears at approximately − 0.30 eV below the Fermi level, comparable with the calculated value − 0.54 eV.[7] In addition, the bottom of the sixth (Λ_6) band is placed at − 1.25 eV, comparable with − 1.30 eV[7] (Fig. 2). Second, in the energy region − 1.0 to − 0.5 eV, the relative contribution of the fourth (Λ_4) band is nearly a factor of 2 larger than the sum of the contributions from the fifth (Λ_5) and sixth (Λ_6) bands.

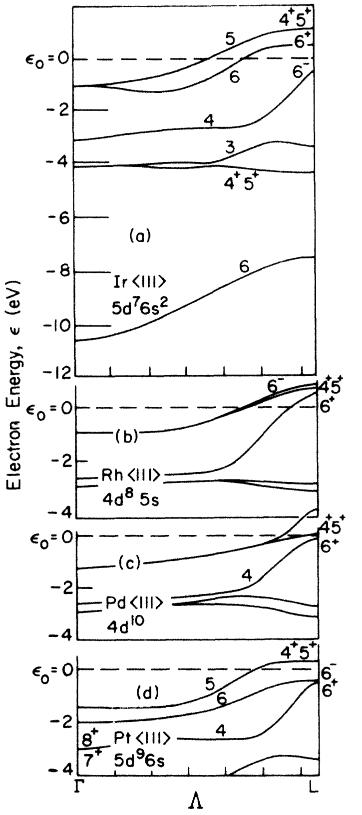

FIG. 2. Sketch of the calculated relativistic energy bands along the Λ direction according to Andersen (Ref. 7) for (a) iridium, (b) rhodium, (c) palladium, and (d) platinum.

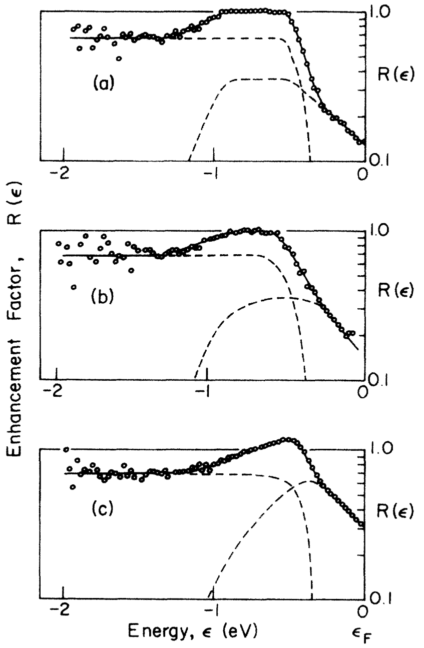

FIG. 3. Enhancement factor $R(\epsilon)$ plotted versus normalized energy ϵ. The decompositions are indicated by the dashed curves. (a) Clean, (b) hydrogen-covered, and (c) nitrogen-covered Ir(111) surfaces at 78°K. Saturation adsorption corresponds to an equivalent monolayer.

Third, there is a pronounced attenuation of the field-emission current associated with the band edges which cannot be satisfactorily explained in terms of experimental factors.[3] Although surface effects on band structure are still controversial, one valid explanation is found in the band-edge compression of the states at the metallic surface, calculated recently.[16-18] Simply stated, the reduction in number of nearest-neighbor atoms for atoms at the surface has the consequence of lowering the local density of states near the band edge with a concomitant peaking near the center of the band relative to that in the bulk.

The spectra for the (111) faces of the other three metals [Figs. 1(b)-1(d)] show similar systematic agreement with the calculated band structure.[7] For rhodium and palladium the L_6^+ level occurs above or very close to the Fermi level; consequently the spectra are free-electron-like nearly up to the Fermi level with relatively less contribution from the d-like t_{2g} bands. For platinum, an attenuated hump for the L_6^+ edge is much less developed than it is for iridium, suggesting less s-p-like character than is indicated by the bulk band structure. It should be noted that the (100) and (110) faces of platinum clearly demonstrate the X_7^+ edge at nearly the predicted value.[6]

Unlike the results obtained for W(100),[11,12] adsorption of saturation monolayers of common gases did not effectively remove the observed structure for Ir(111). To obtain a field-independent representation,[1] the experimental enhancement factor $R(\epsilon)$ is plotted versus energy in Figs. 3(a)-3(c) for the clean, hydrogen-covered, and nitrogen-covered surfaces, respectively, of Ir(111). [$R(\epsilon)$ is obtained from the ratio of the measured energy distribution to the standard FEED curve corrected for uncertainty from instrumental resolution which is then fitted to the fourth-band portion of the experimental curves.] Hydrogen adsorption at 78°K [Fig. 3(b)] tended to reduce the band-edge local density of states with an apparent shift of the composite-band central peak towards a higher energy level. The local density of states shows substantial growth for nitrogen adsorption at 78°K [Fig. 3(c)], an upward energy relocation of the composite band maximum, and a pronounced band-edge compression. A weak, localized bonding occurring between the t_{2g} band states and the virtual levels of these adsorbed gases is consistent with these observed characteristics.[16,18,19]

To facilitate a description of the emission-enhancement plots (Fig. 3), we may rewrite the equation for the field-emission current density in terms of a composite enhancement factor which is a summation over contributions among overlapping bands, $R(\epsilon) \simeq \sum_j n(\epsilon, k_\perp{}^j)$. Here, $n(\epsilon, k_\perp{}^j)$ is a normalized, local density of states in the metal averaged over that small portion of the constant-energy surface in $\mathbf{k}$ space for which the tunneling probability has an appreciable value. In addition to being evaluated at the surface-averaged, classical turning point, $n(\epsilon, k_\perp{}^j)$ is normalized with respect to a one-dimensional local density of states for a free-electron gas. The decomposed curves of Fig. 3(a) indicate a constant of proportionality between the local density of states and that for a free-electron gas except for the band-edge region where $n(\epsilon, k_\perp{}^j)$ appears to be a direct measure of the band-edge compression factor. This approach may provide quantitative information on band contraction at the surface.

These results indicate that the main features of the band structure can be quantitatively reflected in the FEED spectra. Also the surface density of states can be directly attributed to contributions from the surface by comparison to the calculated bulk band structure in those cases where the latter is well defined.

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