37, 1754 (1976).

[6] G. I. Kachen, Jr., W. Clements, and M. Genin, Lawrence Livermore Laboratory Report No. UCRL-50021-72-1, 1972 (unpublished), pp. 110–111; W. L. Kruer and J. M. Dawson, Phys. Fluids 15, 446 (1972).

[7] R. L. Morse and C. W. Nielson, Phys. Fluids 16, 909 (1973); W. M. Manheimer, D. G. Colombant, and B. H. Ripin, Phys. Rev. Lett. 38, 1135 (1977).

[8] D. W. Forslund, J. M. Kindel, K. Lee, E. L. Lindman, and R. L. Morse, Phys. Rev. A 11, 679 (1975); K. G. Estabrook, E. J. Valeo, and W. L. Kruer, Phys. Fluids 18, 1151 (1975).

[9] E. Valeo, W. Kruer, K. Estabrook, B. Langdon, B. Lasinski, C. Max, and J. Thomson, in *Proceedings of the Sixth International Conference on Plasma Physics and Controlled Nuclear Fusion Research, Berchtesgaden, West Germany, 1976* (International Atomic Energy Agency, Vienna, 1976), paper No. IAEA-CN-35/F4; and B. Bezzerides, D. F. DuBois, D. W. Forslund, J. M. Kindel, K. Lee, and E. L. Lindman, *ibid.*, paper No. IAEA-CN-35/F3.

[10] K. G. Estabrook, private communication.

Electronic Structure of Catalytic Metal Clusters Studied by X-Ray Photoemission Spectroscopy

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(Received 7 April 1977)

Pd and Pt clusters on carbon substrates have been studied by x-ray photoemission spectroscopy (XPS). Variations in valence- and core-level spectra with cluster size have been observed. Single-atom centers appear to exist in the d^9s^1 configuration. The d-electron count increases with cluster size, and in the case of Pt a correlation between d-orbital occupation and catalytic activity in electroless nickel deposition is observed.

We have chosen x-ray photoemission spectroscopy (XPS) to study the electronic structure of Pd and Pt nuclei supported on amorphous carbon substrates. The nuclei are prepared by vapor deposition onto the previously evaporated carbon films. Details of sample preparation and variation in cluster-size distribution with metal coverage have been previously reported.[1] The spectra were recorded on a Hewlett-Packard 5950A ESCA (electron spectroscopy for chemical analysis) spectrometer. Binding energies were referenced to the carbon 1s line of the substrate, which was assigned a value of 284.6 eV. This value was consistent with a zero binding energy for the Pd and Pt Fermi edges at high coverage. The valence-band (VB) spectra were corrected by subtraction of the carbon background and inelastic-scattering tail.[2] The corrected VB spectra of Pd and Pt nuclei are shown in Figs. 1 and 2. These spectra cover the range from isolated single atoms to bulklike clusters.[1] The evolution of the bulk spectra occurs in a continuous manner as the coverage is increased and is virtually complete above ~ 3×10^{15} atoms/cm^2. In addition to the VB spectra, we have also measured 3d (4d) core binding energies for Pd (Pt).

Spectra at the lowest coverages will be discussed first since these originate almost completely from single-atom centers.[1] The ground-state free-atom configurations for Pd and Pt are $4d^{10}$ and $5d^96s^1$, respectively.[3] However, in both

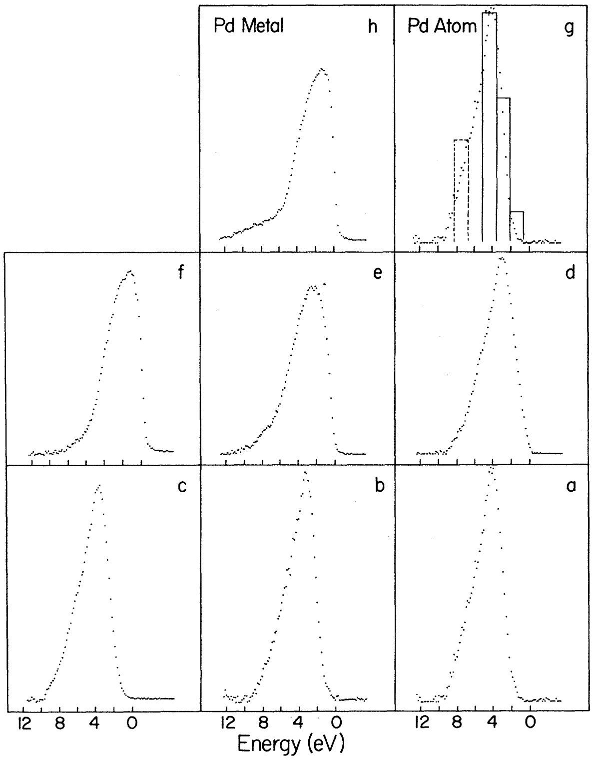

FIG. 1. The XPS spectra of Pd nuclei after background subtraction. The coverages in atoms cm^{-2} are (a) 2×10^{14}; (b) 4×10^{14}; (c) 8×10^{14}; (d) 1.6×10^{15}; (e) 3.1×10^{15}; (f) 6.2×10^{15}; (g) 2×10^{14}; and (h) bulk metal. The histogram in (g) represents the spectral profile for ionization of Pd in the d^9s^1 configuration. The calculated ^2S state is dashed (see text).

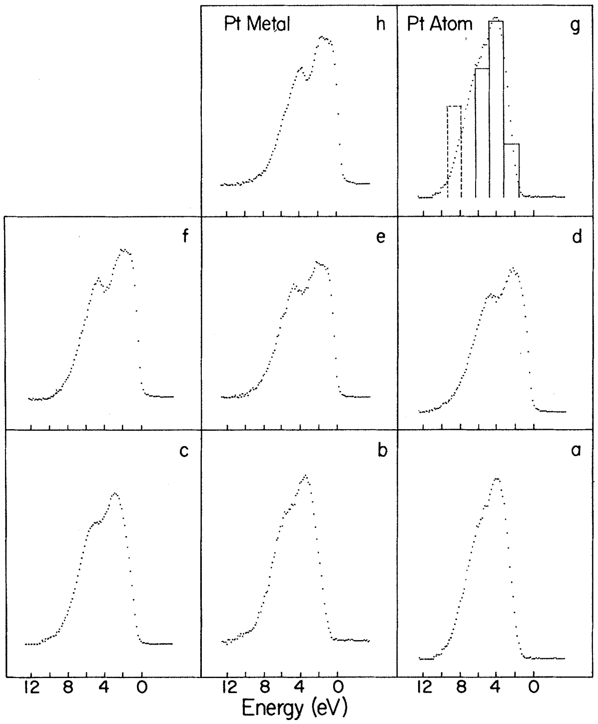

FIG. 2. The XPS spectra of Pt nuclei after background subraction. The coverages in atoms cm^{-2} are (a) 3.8×10^{14}; (b) 7.5×10^{14}; (c) 1.5×10^{15}; (d) 3×10^{15}; (e) 6×10^{15}; (f) 1.2×10^{16}; (g) 3.8×10^{14}; and (h) bulk Pt metal. The histogram in (g) represents the spectral profile for ionization of Pt in the d^9s^1 configuration. The calculated ^2S state is dashed (see text).

Pd and Pt the d^{10} and d^9s^1 configurations are nearly degenerate,[3] and one cannot assume the free-atom configuration in the adsorbed state. In fact, Plummer and Rhodin[4] have shown that both Pd and Pt exist as d^9s^1 atoms when adsorbed on the low-index faces of tungsten. We have come to a similar conclusion for adsorption on the carbon substrate used in this study.

Ionization of a d^{10} initial state would yield $^2D_{5/2}$ and $^2D_{3/2}$ final states separated by only 0.4 eV for Pd and 1.0 eV for Pt. By comparison, the experimental spectra have linewidths FWHM (full width at half-maximum) of 3.5 and 4.7 eV and show structure which is inconsistent with such closely spaced doublets.[5] Ionization of a d-electron from a d^9s^1 configuration gives seven multiplets in the L-S coupling scheme with a total of sixteen components. Prediction of the resulting XPS spectra is complicated by the lack of optical data on the ^2S state of the d^8s^1 configurations.[3] However, the position of this state can be estimated from the energies of measured states by elementary multiplet theory. The intensity for ionization into a given component can be calculated using well-developed theory for open-shell systems.[6] In producing the histograms shown in Figs. 1(g) and 2(g), a ^2D ground state is assumed in which the sublevels are occupied according to their total $(2J+1)$ degeneracies. Intensity from the s electron is neglected because of low ionization cross section. Zero energy is arbitrarily set, and line broadening is approximated by summing the component intensities within each 1.5-eV interval.[5] Since actual line shapes are unknown and linewidths are expected to increase with binding energy and substrate density of states,[7] these histograms are only rough approximations of the actual spectra. The qualitative agreement in band shape and width is considered strong evidence for the d^9s^1 initial state, especially since a d^{10} initial state would yield only the single intense bar at about 4 eV in Figs. 1(g) and 2(g).

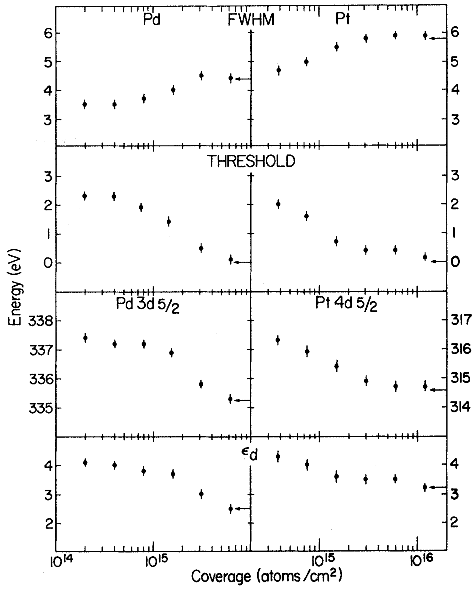

FIG. 3. Variation of valence-band width (FWHM), threshold (low binding energy VB edge), core-level binding energy, and valence-band centroid (ϵ_d) with coverage. Bulk values are indicated by arrows.

The effects of cluster size on electronic structure are manifested by the variations in the VB and core spectra shown graphically in Fig. 3. Changes in linewidths (FWHM) and threshold energy originate from three sources: (i) The spin-orbit interaction may increase slightly because of the renormalization of the d-electron wave functions in going from the free atom to the solid.[8] (ii) The crystal field will split the atomic d levels into a doublet with spacing on the order of 1.5 eV for Pd[9] and 2.5 eV for Pt.[10] (iii) Mixing of the atomic levels throughout the Brillouin zone will cause them to broaden into bands with overall widths of about 5 to 6 eV.[9,10] These latter two factors are almost totally responsible for the increasing line width with particle size and account for a large fraction of the change in threshold energy.

The large variations in core-level binding energies and valence-band centroid, ϵ_d (Fig. 3), are unexpected in view of the relatively small shifts observed in previous studies of silver clusters.[11] Atom-to-metal binding-energy shifts have recently been examined in detail by Watson and Perlman.[12] Their treatment shows that changes in electronic configuration can result in significant binding-energy shifts. In Pt and Pd the supported atoms have d^9s^1 configurations while the bulk metals have approximately 9.6 electrons per atom in the d band.[13-15] Binding-energy shifts expected from such increased d-orbital occupation qualitatively account for the core level and ϵ_d changes in Fig. 3. One can estimate the changes in ϵ_d with orbital occupation by interpolation between the measured ionization potentials of known atomic configurations.[3] For comparison with the experimental ϵ_d, these values must be averaged over all possible final states resulting from a given initial configuration.[6] Again, the absence of experimental data on the $d^8s^1\,{}^2S$ state causes uncertainty in this comparison. In Table I we show the predicted shifts with and without inclusion of the calculated ${}^2S$ energy. Considering the approximations involved, the agreement is reasonably good. These shifts also help substantiate the d^9s^1 assignment for the supported atoms, since a d^{10} configuration would require shifts in the opposite direction. Further evidence of increased d-electron density in larger clusters is seen by an enhanced intensity at the top of the VB as metal coverage increases (Fig. 4). These coverages encompass the region where spectra become characteristic of the bulk metal.

TABLE I. Comparison of observed core- and valence-level shifts with values estimated by interpolation of gas-phase data. Configuration change is assumed to be $4d^95s^1 \rightarrow d^{9.6}s^{0.4}$ (Ref. 15).

	Pd		Pt	
Calculated shift (eV) [a]	2.24 [b]	2.70 [c]	1.51 [b]	2.08 [c]
Core-level shift (eV)	2.1		1.6	
Valence ϵ_d shift (eV)	1.6		1.1	

[a] The ground-state energy was taken as the average energy of the ${}^3D$ state. Ref. 3.

[b] The calculated ${}^2S$ state has not been included. See text.

[c] The calculated ${}^2S$ state has been included.

The origin of these configuration changes in going from atom to metal can be illustrated by the renormalized-atom approach to band structure.[16] In this model, charge neutrality within the Wigner-Seitz (WS) unit cell is achieved by truncating the atomic wave functions at the radius of the cell and renormalizing to the WS sphere. The more charge residing outside the WS sphere, the greater the energy required to compress it. In the case of transition metals, the $(n+1)s$ orbitals are much more diffuse than the nd orbitals, and consequently greater energy would be required to form a solid with higher s-electron occupation. As a result, transition metals generally have lower s-orbital occupation in the metal than in the free atom.

Changes in s- and d-orbital occupations of the type observed in this work may be of considerable importance in understanding "demanding" reactions; that is, catalytic reactions which show increased (specific) rates with decreasing coverage.[17] One such reaction involving the electroless deposition of nickel from solution has been studied in these laboratories. This reaction proceeds spontaneously in the presence of small Pt clusters,[18,19] whereas at higher Pt coverages, the reaction completely quenches. The transition region for catalytic activity coincides with that for increased d-electron occupation shown in Fig. 4. The same reaction with Pd clusters appears to be "nondemanding"[18] and the continued activity

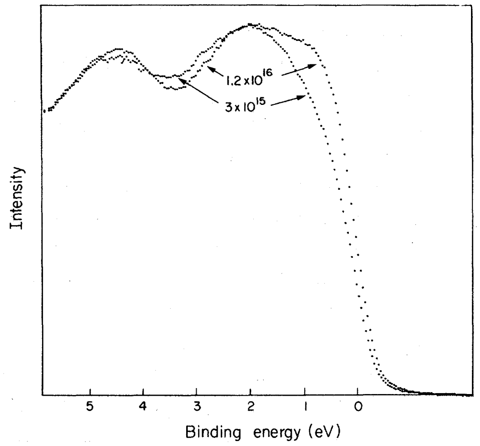

FIG. 4. High-resolution spectra of Pt threshold region at 3×10^{15} and 1.2×10^{16} atoms cm^{-2}.

of larger clusters is not well understood. This behavior may be associated with the higher density of states and lower d-band hybridization at the Fermi level[20] resulting in a higher d-hole density near the occupied portion of the band.

We thank J. F. Hamilton for preparing the samples and for many helpful discussions.

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[1] J. F. Hamilton and P. C. Logel, Thin Solid Films 23, 89 (1974).

[2] At very low coverages, there is no inelastic tail associated with the metal peaks.

[3] C. E. Moore, *Atomic Energy Levels as Derived from Analysis of Optical Spectra*, National Standard Reference Data Series No. 35 (U. S. GPO, Washington, D. C., 1971).

[4] E. W. Plummer and T. N. Rhodin, J. Chem. Phys. 49, 3479 (1968).

[5] For the measured linewidths to result from d^{10} atoms, the substrate-induced broadening would have to be larger than 3 (4) eV for Pd (Pt). In view of the 1.6-eV linewidth measured by Eastman [D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 30, 177 (1973)] for Pd on Ag, such line broadening in the present case seems unrealistic. The fact that the higher-coverage cluster and bulk spectra are nearly identical also suggests that interactions with the substrate are not large.

[6] P. A. Cox, Struc. Bonding (Berlin) 24, 83 (1975).

[7] J. R. Schrieffer, J. Vac. Sci. Technol. 9, 561 (1972).

[8] L. Ley, S. P. Kowalczyk, F. R. McFeely, and D. A. Shirley, Phys. Rev. B 10, 4881 (1974).

[9] C. Y. Fong, J. Phys. F 4, 775 (1974); N. J. Dionne and T. N. Rhodin, Phys. Rev. B 14, 322 (1976).

[10] D. L. Rogers, Phys. Status Solidi (B) 66, K53 (1974); O. K. Anderson, Phys. Rev. B 2, 883 (1970).

[11] M. G. Mason and R. C. Baetzold, J. Chem. Phys. 64, 271 (1976).

[12] R. E. Watson and M. L. Perlman, Struc. Bonding (Berlin) 24, 83 (1975).

[13] F. M. Mueller and M. G. Priestley, Phys. Rev. 148, 638 (1966).

[14] J. B. Ketterson, M. G. Priestley, and J. J. Vuillemin, Phys. Lett. 20, 452 (1966).

[15] An assignment of 9.6 d electrons per atom in the bulk metal is actually an upper limit since hybridization of the d band with the empty s-p conduction states will cause the true d-electron count to be lower.

[16] L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972).

[17] G. C. Bond, in *The Physical Bases for Heterogenous Catalyses*, edited by E. Drauglis and R. I. Jaffee (Plenum, New York, 1975), pp. 53–71; M. Boudart and L. D. Ptak, J. Catal. 5, 446 (1966).

[18] J. F. Hamilton, J. Vac. Sci. Technol. 13, 319 (1976), and to be published.

[19] The minimum size is very reaction dependent and can be as small as two atoms for Pt and Pd (Ref. 18).

[20] Andersen, Ref. 10.

Experimental Determination of the Quasiparticle Energy Distribution in a Nonequilibrium Superconductor

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We have observed sharp structure in the I-V characteristics of Al-AlO$_x$-PbBi tunnel junctions induced by tunnel injection of excess quasiparticles into the Al film. Interpretation of this structure provides information on the form of the steady-state quasiparticle energy distribution, showing that it is highly nonthermal. The data also demonstrate the presence of a branch imbalance in the injected Al film.

Nonequilibrium phenomena in superconductors have attracted considerable attention,[1] both because of their intrinsic interest and because the behavior of superconducting devices such as Josephson weak links is often substantially nonequilibrium in nature. An important feature of the problem is the form of the nonequilibrium quasiparticle and phonon energy distributions, $f(E)$ and $n(\Omega)$, respectively. Experiments on phonon generation and detection using superconducting tunnel junctions and phonon fluorescence in superconductors have provided evidence that the phonon distribution can be highly nonthermal.[2-5] Until very recently, however, the most commonly used models of the nonequilibrium state in superconductors have incorporated modified thermal distributions.[6,7] The experimental evidence has so far been insufficient to distinguish among or against these models, or, for that matter, to rule out "simple heating" to the satisfaction of