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Evolution of band structure in gold clusters as studied by photoemission

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Photoemission studies of gold clusters with variable photon energies, $16 \leq h\nu \leq 25$ eV and $h\nu = 1486.6$ eV, are used to follow the evolution of band structure with cluster size. We clearly show that a minimum size in excess of 100 atoms is required to observe any of the spectral modulation effects characteristic of the bulk metal.

Studies of the electronic structure of small transition metal clusters have become more tractable for theoreticians and experimentalists. Several theoretical studies[1] and experimental photoemission results[2-4] of supported clusters have been reported. These experiments have utilized photon energies ($h\nu$'s) of 21.2 eV or higher. They have also looked only at 3*d* and 4*d* valence-band (VB) metals where spin-orbit splittings are small and the bulk-metal bands are closely spaced. Because of these limitations, the evolution of electronic structure, from atomiclike to band-structure-like, has not been clearly demonstrated.

We have chosen to study gold (5*d* VB), supported on amorphous carbon substrates, primarily within the photon-energy range from 16 to 25 eV. Low $h\nu$'s are important because of their spectral sensitivity to band-structure effects in polycrystalline (i.e., randomly oriented) materials.[5] Most of these modulation effects occur at $h\nu$'s less than 21.2 eV and thus were not observed in previous studies of metal clusters. 5*d* VB's are important to study because they exhibit much *d*-type spectral structure over a wide range of energies, typically ~6 eV, whereas the 3*d* and 4*d* VB's show little structure over a narrower width, ~3 eV. In this report we present $h\nu$-dependent spectra of gold clusters whose sizes range from single atoms to those with bulklike properties. In addition, we observe for the first time a detailed evolution of band structure with particle size and determine quite accurately the minimum number of atoms necessary for bulklike electronic structure.

Experiments were done with synchrotron radiation at the Tantalus I storage ring at the Physical Sciences Labratory, University of Wisconsin, as well as with "in-house" Ne I, He I, and monochromatic Al$K\alpha$ radiation. uv work was done with cylindrical mirror analyzers and x-ray photoemission spectroscopy (XPS) work with a Hewlett-Packard ESCA spectrometer. The gold clusters were prepared *in situ*, $\lesssim 1 \times 10^{-9}$ Torr, by evaporation onto amorphous carbon substrates which were cleaned by argon-ion etching without subsequent annealing. Spectra were recorded at low $h\nu$'s with a resolution of 0.3 eV and XPS energies with a resolution of ~0.5 eV. Coverages were controlled by a quartz-crystal deposition monitor and verified by XPS analysis of the Au 4*f* and C 1*s* intensities as compared to known standards. Spectra of the Au clusters on carbon and the appropriately normalized spectra of the clean carbon were then subtracted to yield spectra characteristic of the clusters themselves.

Spectra of bulk polycrystalline gold are presented in Fig. 2(e). They are in substantial agreement with the data of Eastman and Grobman.[6] In general, the spectra can be divided into three regions: (1) the *s-p* band between the Fermi level, $E_F = 0$, and 2 eV (2) the first *d* band between 2 and 4 eV and (3) the second *d* band between 5 and 8 eV. Both the first and second *d* bands show significant modulation effects. The low binding-energy (BE) component of the first d band is the most intense for $h\nu < 20$ eV, whereas the higher BE component is more intense for $20 \leqslant h\nu \leqslant 24$ eV. As a result, the centroid of this band moves to higher binding energy as $h\nu$ is increased. Even greater changes are seen in the modulation of the second *d* band intensity with $h\nu$. At $h\nu \leqslant 20$ eV the second d band peak height is considerably smaller than that of the first. However, at $h\nu \geqslant 21.2$ eV the peak heights of the two bands become quite comparable. Along with this change in intensity, the centroid of the second *d* band moves to lower binding energy with increasing $h\nu$. The opposing behavior of the *d* band centroids causes the splitting between the first and second *d* bands to be $h\nu$ dependent and to decrease with increasing $h\nu$.

The $h\nu$ dependence of these spectra is a direct result of the periodic structure in the bulk metal.

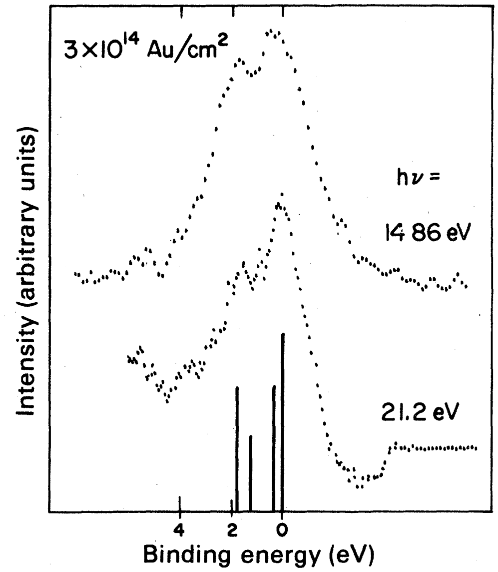

FIG. 1. Al$K\alpha$ and He I difference spectra of gold atoms with carbon background subtracted. The histogram shows the energy levels of the free Au$^+$ ($5d^96s^1$) ion with the zero arbitrarily adjusted and the intensities determined by the total spin-orbit degeneracies.

In a small cluster the crystal momentum has no meaning and k is not a valid quantum number. Hence, the spectra of small clusters should be almost independent of excitation energy, showing only small variations due primarily to $h\nu$-dependent ionization cross sections. Small-cluster spectra should also correlate well with the occupied density of states. This is in fact observed at very low coverages where the spectra (Fig. 1) quantitatively reproduce the density of states for a free gold atom[7] with $d^{10}s^1$ valence configuration.

Since spectral modulation with $h\nu$ is dependent upon bulklike periodic structure, its presence or absence should be a sensitive test for the bulk nature of a cluster. In Fig. 2 we show spectra at $16 \leq h\nu \leq 25$ eV and $h\nu = 1486.6$ eV for five difent coverages of gold, including bulk metal. These coverages span up to the range where modulation effects become significant. At the lowest coverage, 8×10^{14} atoms cm^{-2}, slight intensity variations are observed but are small relative to those exhibited by the bulk. Peak positions remain constant as a function of $h\nu$. The drop in intensity of the second d band at $h\nu \leq 16.8$ eV may well be due to uncertainty in

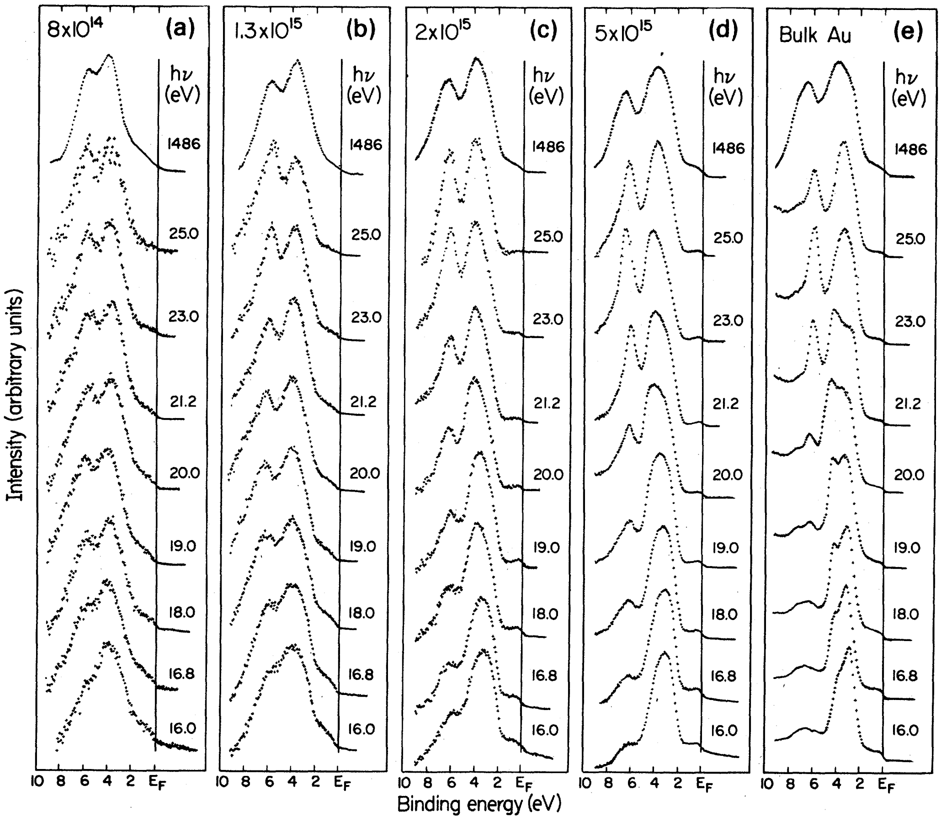

FIG. 2. Difference spectra of gold clusters with carbon background subtracted.

background subtraction because of significant overlap between the Au 5*d* levels and the intense inelastic electron distribution (peak of the secondary electron energy distribution). At higher coverages this interference is less severe. Splittings and intensities change continuously with increased coverage. Above ~2×10^{15} atoms cm^{-2} we observe the onset of bulklike spectral behavior; however, there are still obvious differences. At low $h\nu$ the d band splitting is less than bulk and the second *d* band is much too intense. As coverages are increased, both of these features become more bulklike.

The *d* band splittings are shown graphically in Fig. 3 as a function of coverage. These data are taken at three photon energies, Ne I (16.8), He I (21.2), and Al$K\alpha$ (1486.6), and include results from both laboratory and synchrotron sources. For coverages $<1\times10^{15}$ atoms cm^{-2}, the *d* splitting is coverage dependent but independent of $h\nu$. In this range the clusters are more analogous to a large molecule than to a small segment of bulk metal. At higher coverages modulation effects are observed, with large differences between Ne I and higher-energy excitations. At 5×10^{15} atoms cm^{-2}, bulk splittings are found at all three $h\nu$'s. Based solely on this criterion, the spectra appear bulklike. However, a closer examination shows that neither the intensities nor the structural detail is characteristic of bulk metal. This is clearly seen in Fig. 4, where the intensity ratio of the first and second *d* bands is plotted against $h\nu$. Almost no intensity-modulation effects are observed up to 1.3×10^{15} atoms cm^{-2}. This agrees with the data in Fig. 3 and with the molecular nature of the clusters. Modulations are observed at coverages $\geq2\times10^{15}$ but they are not completely bulklike even at 5×10^{15} atoms cm^{-2}.

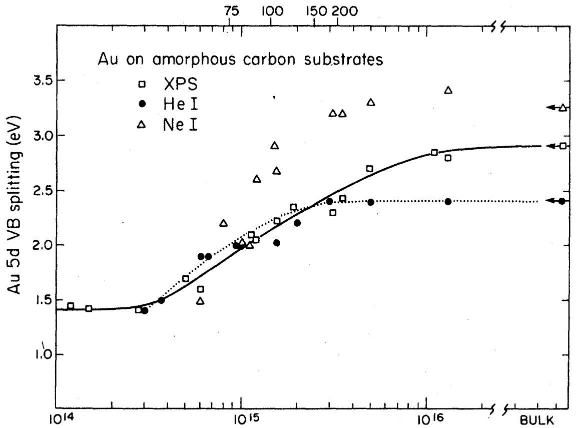

FIG. 3. Measured 5*d* splitting at 1486.6, 21.2, and 16.8 eV. Numbers at top indicate the approximate number of atoms per cluster. Arrows indicate measured bulk values.

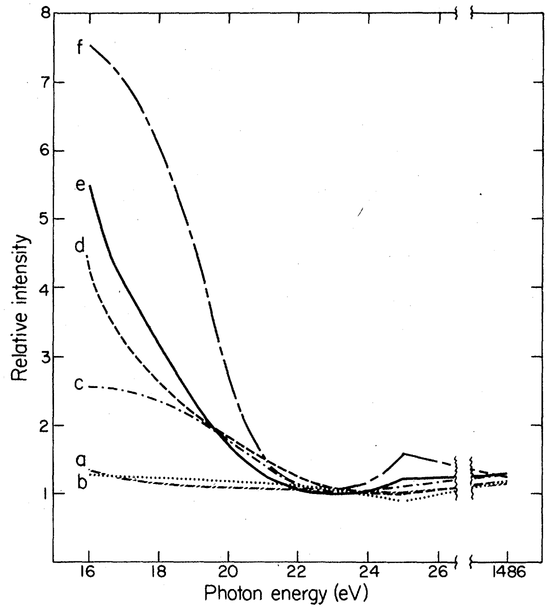

FIG. 4. Variations in relative peak heights of the first and second *d* bands with photon energy. For clarity, smooth curves have replaced the actual data points as obtained from Fig. 2. Coverages in atoms cm^{-2} are (a) 8×10^{14}, (b) 1.3×10^{15}, (c) 2.1×10^{15}, (d) 2.5×10^{15}, (e) 5×10^{15}, and (f) bulk.

Transmission electron micrographs of clusters at 2×10^{15} atoms cm^{-2} show an average diameter of ~19 Å, which corresponds to slightly more than 100 atoms.[8] At 5×10^{15} atoms cm^{-2}, where the bulk splitting is first achieved, the nuclei have begun to coalesce and the average cluster contains several hundred atoms.[9] It is clear that to achieve a completely bulk spectrum, a cluster must become very large. Even for a large cluster or thin film, a significant fraction of atoms is on the surface.

Surface and bulk atoms differ in such properties as net charge, local density of states,[1] and vibrational amplitude.[10] All such factors can contribute to a broadening of spectral shapes. Specifically, enhanced vibrational motion can cause a breakdown in the *k*-conserving direct-transition mechanism of photoemission.[11,12] These factors may largely account for the slow convergence of cluster spectra to bulk.

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