Ultraviolet Photoelectron Spectra of Mass-Selected Copper Clusters: Evolution of the 3*d* Band

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Ultraviolet photoelectron spectra (UPS) have been measured for bare unsupported copper clusters in the 1–410-atom size range as mass selected from a supersonic, negatively charged, cluster-ion beam. Using an F_2 excimer laser at 7.9 eV, the UPS patterns display the evolution of the 3*d* band structure as a function of cluster size. Clusters larger than a few atoms were found to display an increasingly sharp feature at the onset of the 3*d* band similar to that seen for bulk copper UPS at low photon energies, suggesting that these larger clusters may already be crystalline.

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One of the more fruitful developments in cluster science over the past decade has been the success of the shell model for metal clusters.[1] For many simple metals such as sodium, aluminum, or copper the electronic structure near the top of the occupied cluster orbitals (i.e., near the "Fermi energy" of the cluster) appears to be well described by a simple shell model similar to that of nuclear physics. The physical picture here is essentially the same as the free-electron theory of bulk metals, but now with spheroidal boundary conditions at the surface of the cluster. In addition to cluster abundance and ionization-potential measurements of other groups,[1] ultraviolet photoelectron spectra (UPS) of individual mass-selected negative cluster ions performed recently in our laboratory have provided excellent support of this simple shell model for small clusters of a variety of metals.[2,3]

While we find these results impressive, it is still true that the electronic structure being probed is only that of the most weakly bound electrons. Given the success of the shell model near the Fermi energy of the cluster, a reasonable next question is how much deeper down into the band structure of these metal clusters can we probe and understand. For example, in the case of copper, which is certainly one of the most studied and well understood of all bulk metals,[4–7] there is the question of how the 3*d* orbitals of the atoms combine in the clusters, and how the band of cluster levels derived from these 3*d* orbitals evolves to form the 3*d* band of Bloch waves in the extended crystalline solid.

Wertheim has recently reviewed progress in this difficult field.[8] Of particular relevance is an impressive early UPS study of copper clusters supported on carbon films reported nearly a decade ago by Baetzold.[9] While such experiments with supported clusters have been informative, there are unavoidable complications involving the detailed effects of the support and the size distribution of the clusters.[10] The experiment discussed below avoids both of these complications through use of a mass-selected beam of bare, unsupported clusters cooled in a supersonic expansion.

The apparatus used was similar to that of earlier UPS publications from the cluster group at Rice University.[2,3,11,12] Briefly, the clusters were prepared by laser vaporization of a copper rod mounted in a pulsed supersonic nozzle. In order to increase cooling and to aid formation of larger clusters, our nozzle was redesigned such that the laser-generated copper-vapor plume was ejected directly into the intersection of two synchronized neon-gas pulses from opposing fast pulsed valves. The cluster-neon mixture then traveled down a 10° stainless-steel expansion cone prior to expanding as a supersonic free jet into a vacuum chamber. As in earlier cluster UPS work from this laboratory, an ArF excimer laser (3 mJ/cm^2) was directed into the 10° supersonic expansion cone to generate a cluster-ion plasma which was then cooled by subsequent collisions in the expansion. We calculate that the clusters should have received roughly 1000 thermalizing collisions with the neon carrier gas after the ArF-excimer-laser excitation. Considering the number of these collisions and the observed mass-independent arrival time of all clusters 1.2 m downstream in the ion-beam extraction region of the supersonic cluster-beam apparatus, we expect the internal temperatures of these clusters to have been less than 300 K, perhaps much less.

The negative cluster beam was extracted at 1 keV into a time-of-flight mass spectrometer. Clusters up to 80 copper atoms were individually mass selected and decelerated. Above 80 atoms the mass resolution was insufficient to separate individual clusters, but the stability and accuracy of the mass calibration was sufficient to determine the size of the largest cluster reported here (Cu_{410}^-) to within a few atoms. Care was taken to purify the carrier gas from all reactive contaminants by passing the gas over a bed of molecular sieve held at a temperature of 77 K, and by extensively baking and purging all nozzle components. Mass analysis of the negatively charged copper clusters in the 1–80-atom mass range showed the level of oxide contamination was below 10%. We presume that the larger clusters were similarly clean.

The UPS data discussed below were taken with the

output of an F_2 excimer laser beam (157 nm, 7.9 eV) collimated to a 3-mm-diam waist with a fluence of roughly 100 mJ/cm^2 intersecting the mass-selected cluster ions in the source region of a magnetic time-of-flight photoelectron spectrometer of special design.[11] Calibration of this spectrometer was made with the known UPS spectra[13,14] of Cu^- and Au^-. All the spectra reported here have been digitally smoothed with a 0.150-eV square window.

Our principal results are summarized in Fig. 1. Here we show the UPS patterns recorded for a sampling of mass-selected negative copper clusters ranging from the single atom (top) to a cluster with 410 atoms (bottom). To our knowledge this figure provides the first calibrated UPS view of the evolution of electronic band structure for any metal taken at high enough photon energy to probe the 3*d* band.

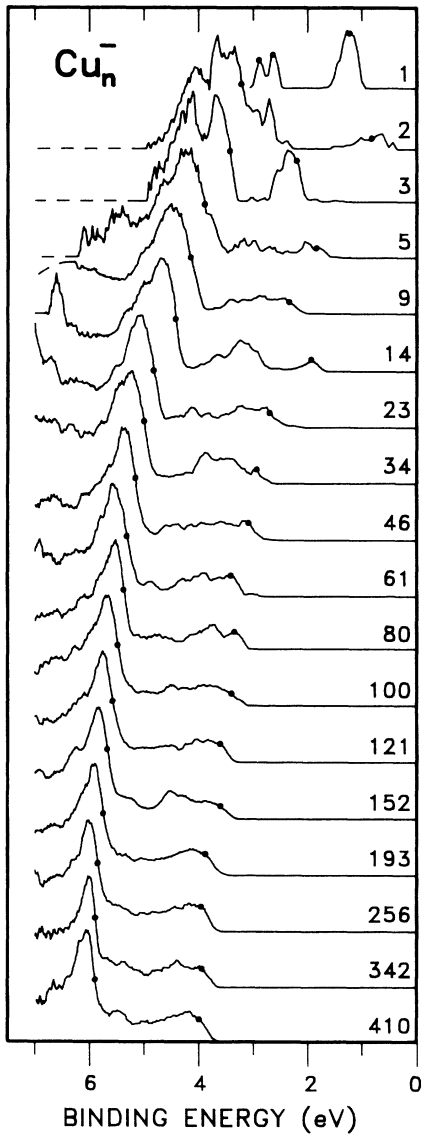

FIG. 1. UPS of negative copper clusters in the 1–410-atom size range mass selected from a supersonic cluster beam, taken with an F_2 excimer laser at 7.9 eV.

By looking at the threshold for photoelectron ejection, one has a direct estimate of the electron affinity of the corresponding neutral version of these negatively charged clusters. For clusters below 42 atoms, we already have published such measurements for copper using lower-energy photodetachment lasers,[2] and for clusters below 11 atoms, high-resolution photoelectron spectra have been published by Leopold, Ho, and Lineberger.[14] Now with the new neon cluster source such measurements can be extended to well over 400 atoms. Taking rough corrections for instrument resolution we have estimated these detachment thresholds at the positions marked with the black dots in Fig. 1. In Fig. 2, we have plotted these as a function of the inverse cluster radius ($1/R$, where R is approximated as the atomic radius of a copper atom in the bulk fcc lattice multiplied by the cube root of the number of atoms in the cluster[14]).

The intricate variations seen in Figs. 1 and 2 in the electron affinities of the small clusters have been shown in earlier publications to be in detailed agreement with the predictions of a simple shell model. For example, the isolated initial feature seen in Fig. 1 for the Cu_{14}^- cluster is nicely explained as a subshell closing. Note that at the 410-atom cluster the electron affinity is now within 0.6 eV of the bulk work function. As discussed in recent metal-cluster literature,[15] most of this shift of electron affinity with cluster size is due to an electrostatic effect, having little to do with the detailed electronic level structure of the cluster.

Roughly 2 eV higher than the weak initial features of the evolving 4*s* band, there is a large peak which moves smoothly with cluster size. For the small clusters its position merges smoothly to the position of the $^2D_{5/2}$ and

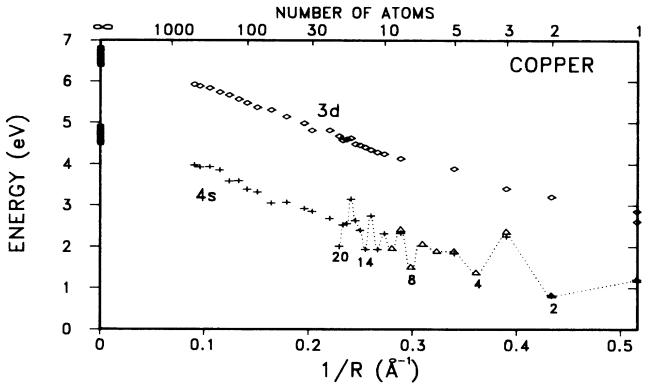

FIG. 2. Electron affinities and 3*d*-band-energy onsets of copper clusters as a function of $1/R$ (see text). Open-triangle data are taken from Ref. 13. The black solid bars on the left-hand side refer to the range of work functions (and corresponding 3*d*-band onsets) measured for the (100), (110), and (111) surface planes of bulk copper.

$^2D_{3/2}$ peaks of the copper atom. For the large clusters, allowing for a 0.6-eV shift to match the work function, the large peak matches well with the sharp onset of the $3d$ band in the UPS of bulk copper.[15-18] For all clusters, therefore, it seems safe to attribute this feature to the photodetachment of primarily $3d$-type electrons, and to choose the rising edge of this feature to be a measure of the top of the "$3d$ band." Taking half the peak height as the $3d$ onset, we have marked these energies both in Figs. 1 and 2.

Note that unlike the large size-dependent variations associated with the $4s$ electrons, the $3d$ features shift monotonically with the cluster size, consistent with the different valence nature of these spectral features. The onset of the UPS is governed by the delocalized valence $4s$ electrons and their energy levels depend sensitively on the surface size and shape of the cluster. In contrast, the $3d$ electrons are more corelike and should be only mildly influenced by the details of the cluster surface.

Figure 3 shows for a typical cluster the dependence of the observed UPS pattern upon photodetachment laser wavelength. Note that there always seems to be a substantial photoelectron signal within 1 eV of the maximum detectable binding energy. The greater part of these electrons appears to come from the cluster equivalent of inelastic electron-electron and electron-phonon scattering, which is always seen in bulk and surface photoelectron spectroscopy. This phenomenon was responsible for our inability to cleanly detect the $3d$ band in our earlier work with photon energies of 4.8 and 6.4 eV.[2,12] To our knowledge this is the first demonstration of such a characteristic bulk scattering even in a molecule. Also evident here is the expected wavelength dependence of the relative cross sections for photodetachment of the $3d$ and $4s$ photoelectrons.

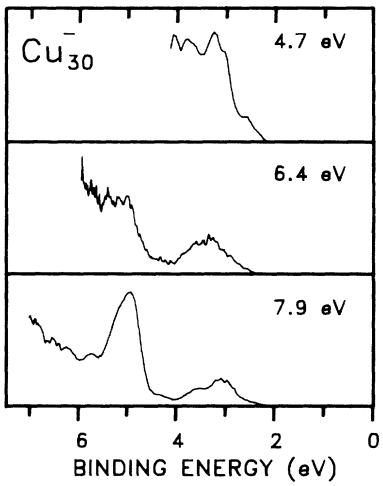

FIG. 3. UPS of Cu_{30}^- mass selected from a supersonic cluster beam, taken with three different photodetachment laser energies.

An intriguing aspect of these UPS spectra is that this feature we attribute to the beginning of the $3d$ band actually narrows as a function of increasing cluster size. We note that the fast-rising $3d$ onset for the large clusters is quite similar to the UPS of bulk copper, particularly as shown in an experiment by Smith with cesiated copper using photon energies as low as 6 eV.[16] Smith observed sharp leading-edge structure in agreement with the energy distribution of the joint density of states deduced from bulk band-structure calculations. He also established that this sharpness derives from a peak in the density of states at the top of the occupied $3d$ band. While it is clear that this strong UPS feature at the top of the $3d$ band sharpens with increasing cluster size, these experiments do not yet permit a measurement of the overall $3d$-band width. That measurement will require substantially higher photon energies than the 7.9-eV F_2 excimer laser used here.

Extensive evidence from supported-gold- and -copper-cluster experiments with electron microscopy[19,20] and extended x-ray-absorption fine-structure spectroscopy,[21] as well as experiments on unsupported clusters with electron diffraction,[22] now exists which establishes that clusters in the 100–1000-atom size range often assume nearly perfect internal crystalline structure. It appears likely, therefore, that the larger copper clusters in this UPS study have well-formed crystalline inner regions. For example, assuming the normal lattice spacing of bulk copper, the diameter of a 410-atom cluster would be 3 nm across with about 50% of the atoms on the "inside" of the cluster. Since the mean free paths of electrons in bulk copper at the energies involved in these UPS experiments are also close to 3 nm,[23] it is reasonable that the UPS pattern for a cluster like Cu_{410}^- would begin to display features of the $3d$ band structure of the bulk.

It will be interesting to see how well such reasoning holds up as this new, direct probe of large, unperturbed mass-selected clusters is extended and compared with detailed theory.

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