Electronic Structure of Small Titanium Clusters: Emergence and Evolution of the 3d Band

Hongbin Wu, Sunil R. Desai, and Lai-Sheng Wang*

Department of Physics, Washington State University, Richland, Washington 99352
and Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, MS K2-14, P.O. Box 999,
Richland, Washington 99352

The electronic structure of titanium clusters (Ti_n, $n = 3-65$) is probed by size-selected anion photoelectron spectroscopy. It is observed that the 3d band emerges at the eight-atom cluster beyond which the d band broadens and evolves toward that of the bulk. The electronic structure of the titanium clusters is found to become bulklike at relatively small cluster sizes. This is discussed in terms of the delocalization of the titanium 3d orbitals and the implications for the cluster structures.

It remains a significant goal in cluster physics to understand the evolution of cluster electronic structure from that of the atoms to the bulk [1]. A central question lies at when and how electrons forming bonds in small clusters are transformed to bands in solids. Over the past few years, photoelectron spectroscopy (PES) of size-selected anions has emerged as a powerful experimental technique to probe the electronic structure of metal and semiconductor clusters [2–7]. In such PES experiments, occupied energy levels or density of states (DOS) of neutral clusters are obtained directly from electron detachment of the corresponding negatively charged clusters. A large number of these experiments have been focused on simple metal systems [8–12], whose electronic structures can be well described by the shell model [13]. Relatively few PES experiments [14–16] have been directed at the transition metals (TM's) due to their enormous complexity even though the TM clusters are more technologically important and the chemical and magnetic properties of several late TM cluster systems have been extensively investigated.

Studies of the electronic structures of TM clusters have thus far been focused on the dimer systems on the promise that the understanding of the diatomics will help understand the larger systems [4,17–20]. However, even the dimers still pose tremendous challenges to *ab initio* calculations and are still not completely understood [18]. The expectation for the larger clusters is that their complexity may prevent any discrete electronic energy level information to be obtained from a PES experiment. However, our recent PES study on iron clusters reveals sharp spectral features for the smaller clusters and well-resolved features for cluster size up to 23 atoms [16]. The experiments provide important information about the electronic structure of the clusters and reveal a clear correlation between the electronic structure and the chemical reactivity. The iron clusters are considered to be more complicated since the atom has many d electrons and the clusters all exhibit ferromagnetic coupling. We study the earlier TM clusters to probe how the different

3d occupations affect the cluster electronic structure and their evolution towards the bulk.

In this Letter, we report the first PES study on small titanium clusters, Ti_n ($n = 3-65$). Besides the diatomics [20], the only previous study on the titanium clusters is a collision-induced dissociation experiment on the positive clusters, Ti_n^+ ($n = 2-22$), by Lian, Su, and Armentrout [21]. With only two d electrons, it is expected that the electronic structure of the small titanium clusters would be simpler than that of the iron clusters, and much more sharp spectral features should be resolved for a wide cluster size. Much to our surprise, sharp spectral features are only observed to about $n = 8$, beyond which the spectral features appear to congest to a broad feature near the Fermi level and its width increases with cluster size. This is interpreted as the emergence of the 3d band. Thus the electronic structure of the titanium clusters appears to behave bulklike at rather small sizes.

The experiments are performed with an apparatus that couples a laser vaporization cluster source and a magnetic bottle time-of-flight (MTOF) photoelectron spectrometer [5,22]. The details of this apparatus have been described elsewhere [16]. Briefly, a titanium disk target is vaporized into an intense helium carrier gas pulse, producing the desired clusters. Care is taken to minimize oxide contamination [16]. The cluster-gas mixture undergoes a supersonic expansion, forming a cold and collimated cluster beam by a skimmer. The negatively charged clusters present in the cluster beam are extracted perpendicularly into a TOF mass analyzer. The clusters of interest are selected by a mass gate and decelerated before interacting with a detachment laser beam from the third (355 nm, 3.49 eV) or fourth (266 nm, 4.66 eV) harmonic of a Nd:YAG laser. Photoelectron TOF spectra are measured for the selected clusters, typically averaging between 10 000 and 30 000 laser shots at 10 Hz repetition rate. At 266 nm detachment wavelength, there is substantial low-energy electron background due to scattered photons interacting with the surfaces near the detachment zone. Therefore

the 266 nm spectra are all taken at 20 Hz with the cluster beam on and off at alternating laser shots for background subtraction. The electron TOF spectra are converted to electron kinetic energy distributions, calibrated with the known spectrum of the Cu^- anion and smoothed with a 10 meV square window function. The kinetic energy spectra are subtracted from the photon energy to obtain the binding energy spectra presented. Our MTOF spectrometer has an energy resolution of about 30 meV at 1 eV electron kinetic energy as measured from the spectrum of Cu^- with full deceleration on the Cu^- anion [16]. The resolution (ΔE) of the TOF analyzer is best for low energy electrons and is proportional to $Ek^{3/2}$, where Ek is the electron kinetic energy.

Our major results are summarized in Fig. 1, which shows collectively all the PES spectra from Ti_3^- to Ti_{65}^-, taken at 4.66 eV photon energy. Discrete spectral features are observed for Ti_{3-8}^-. The spectra in this size range vary from one cluster to the other, reflecting their molecular nature. Starting from Ti_8^-, one prominent feature appears near the detachment threshold and the spectra begin to show similarities. No sharp features are observed beyond Ti_8^- and the discrete features resolved for the smaller clusters seem to congest into the broad feature, whose width increases with cluster size. Interestingly, this broad
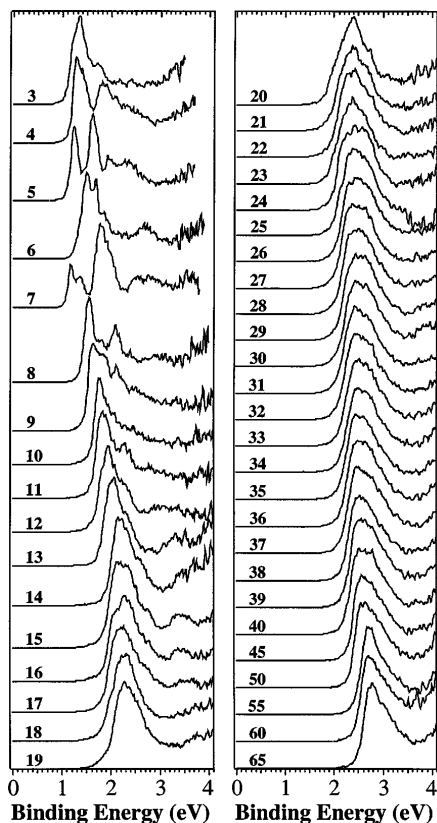
feature becomes quite narrow for Ti_{55}^- and broadens again for the higher clusters. The spikes at the high binding energy side are due to statistical noises, part of which is caused by the imperfect background subtraction.

We also obtained PES spectra for Ti_3^- to Ti_{26}^- at 3.49 eV photon energy with slightly better resolution. Except that the first peak of Ti_4^- is resolved into three partially overlapped features, all the other spectra are qualitatively the same and no more discrete features are observed than that shown in Fig. 1.

The spectra (Fig. 1) represent transitions from the ground state of the negative clusters to the ground state and excited states of the neutral clusters. In a single particle approximation, they can also be viewed as the density of states of the clusters. The detachment threshold yields the electron affinity (EA) of the corresponding neutral cluster. When a sharp threshold feature is observed, the EA can be determined within 0.05 eV. Our estimates of the EAs for the Ti_n ($n = 3-65$) clusters are plotted in Fig. 2. The uncertainty of the EA values is within 0.08 eV for the broad features, but the relative changes for the different cluster sizes are seen clearly in Figs. 1 and 2. Ti_7 has a particularly low EA. The EAs for Ti_8 and above show roughly a monotonic increase and should approach the bulk work function (4.33 eV) at the infinitive size limit. For metallic clusters, the threshold level will evolve into the Fermi level of the bulk crystal, and the PES spectra should eventually resemble the bulk valence photoemission spectrum of titanium.

Our most striking observation is the spectral change from Ti_7^- to Ti_8^- and the appearance that after Ti_8^- all the spectral features seem to be congested into a broad band. This broad feature is already quite similar to the bulk titanium valence photoemission spectrum, which shows a single broad feature near the Fermi level with a width (FWHM) of about 2 eV due to the $3d$ band [23]. The cluster spectral feature broadens as a function of the
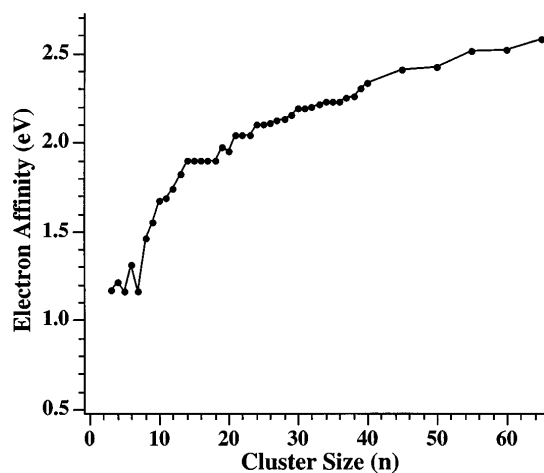

FIG. 1. Photoelectron spectra of size-selected Ti_n^- ($n = 3-65$) clusters at 4.66 eV detachment energy. Note the change from $n = 7$ to 8 and the spectral similarity thereafter.

FIG. 2. The electron affinity of the Ti_n clusters as a function of cluster size.

cluster size and attains a width of about 1 eV in the range between Ti_{20} and Ti_{50}. Ti_{55} exhibits a particularly narrow band, and it broadens again at larger cluster sizes. It is anticipated that this feature will broaden and evolve into the bulk valence photoemission feature as the cluster size is continuously increased. Therefore we conclude that the bulk $3d$ band already emerges near Ti_8 and evolves towards bulk as the cluster size increases.

The titanium clusters seem to behave quite different compared to the later TM clusters. For example, sharp spectral features are observed for cluster sizes larger than 20 atoms for chromium [24] and iron clusters [16]. We expected that more sharp spectral features would be observed for the titanium cluster systems because of the reduced number of $3d$ electrons. However, the opposite is true and the spectra become broad and bulklike at quite a small size. This suggests that the electronic structure of the titanium clusters is either relatively insensitive to the cluster size or the clusters already assume certain structure reminiscent of the bulk lattice.

The spherical drop model has been used extensively to assess the evolution of metallic cluster properties toward that of the bulk [25,26]. This model predicts a $1/R$ (R is the cluster radius) dependence of cluster properties (ionization potential, EA, and cohesive energy) when the clusters become metallic and can be approximated by a spherical drop of radius R. Previous dissociation experiments on the positive titanium clusters indicate that the cluster cohesive energies change approximately linearly with $n^{-1/3}$ (proportional to $1/R$) after $n = 6$ and extrapolate to a value very close to the bulk cohesive energy at infinitive n [21]. The EA values are plotted similarly against $n^{-1/3}$ in Fig. 3. The straight line is a prediction from the classical spherical drop model, $EA = WF - \beta(e^2/R)$, where WF is the bulk work function (4.33 eV) and β is taken as $5/8$ [26]. The cluster radius R is approximated by the covalent radius

of Ti (1.32 Å) times $n^{1/3}$. It is seen the EAs increase monotonically toward the bulk work function starting from Ti_8, and the EAs of the larger clusters are described by the spherical drop model quite well. The deviation from this model at smaller cluster size is expected due to quantum mechanical effects, as discussed in detail recently [26]. This suggests that indeed the titanium clusters are becoming metallic at relatively small sizes and can be approximated by metallic spheres. Comparatively, simple metal clusters such as the alkalis and the coinage metals are known to be described well by the spherical drop model modified by the shell effects [8].

Further insight into the electronic structure of the titanium clusters may be obtained by considering the differences between titanium and the late transition metals and the variation of the $3d$ orbitals across the first transition series. The major difference is that the $3d$ orbitals of titanium are more delocalized. The size of the $3d$ orbitals in the first TM series decreases from the left to the right as a result of the increased nuclear charge. The $3d$ orbitals of titanium are completely valence orbitals that participate in chemical bonding in all the titanium chemical compounds. The d orbitals of titanium are expected to be substantially delocalized and overlap with neighboring atoms in the clusters. Since there are fewer d electrons in titanium, there will be no antibonding d orbitals filled, facilitating a more close-packed and more tightly bound clusters. Indeed, the dissociation energies of the small Ti_n^+ clusters are among the highest in the first row TM clusters, and highly close-packed icosahedral structures have been suggested for certain titanium clusters [21]. Our observation of a narrower PES feature (Fig. 1) for Ti_{55}^- is also consistent with a highly symmetric icosahedral structure for this cluster. Therefore we attribute the rapid convergence of the titanium cluster electronic structure toward that of the bulk to the strong delocalization of the $3d$ orbitals and the anticipated close-packed cluster structures.

In conclusion, we observed that the photoelectron spectra of the small titanium clusters converge to a bulklike feature rapidly as a function of cluster size. The $3d$ band is found to appear at Ti_8 and evolves toward the bulk with increasing cluster size. This behavior of the electronic structure of the titanium clusters is interpreted as due to the $3d$ orbital delocalization forming probably rather close-packed structures. Very recently, it has been possible to simulate PES spectra of small silicon and copper clusters and to obtain cluster structures definitively by comparing the simulations to the experimental PES spectra [27]. The present work can be used similarly and therefore provides an important base to understand not only the electronic but also the geometric structures of the small titanium clusters.
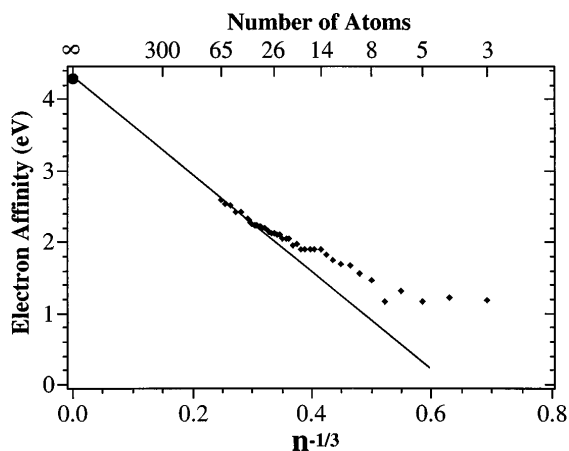
FIG. 3. The electron affinity of the Ti_n clusters versus $n^{-1/3}$. The straight line is the prediction from the classical spherical drop model (see text). The big dot indicates the bulk work function.

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*To whom correspondence should be addressed.

[1] See, for example, *Physics and Chemistry of Finite Systems: From Clusters to Crystals,* edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer Academic Publishers, Boston, 1992), Vols. I&II.

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