Particle-Size–Induced Valence Changes in Samarium Clusters

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Samarium clusters exhibit mixed-valence behavior which is sensitive to particle size. X-ray photoemission and ultraviolet photoelectron spectroscopy data show samarium to be primarily divalent ($4f^6$) at small particle size. The trivalent state ($4f^5$) becomes progressively more abundant with increasing size, becoming the dominant state for the bulk metal. These results are interpreted in terms of band narrowing due to reduced surface coordination, which is more dominant than surface tension effects in establishing the valence of small samarium clusters.

Changes in electronic configuration or orbital occupation numbers with particle size have been predicted theoretically[1] and have been used as a basis for interpreting the photoemission spectra from clusters of platinum-group metals.[2] That electronic configurations will normally change in going from an atom to a bulk metal is clear at the extremes of size. Free atoms have integral configurations, whereas bulk metals, in general, do not. However, size-dependent changes in core-level binding energies or valence-level intensities, such as observed in photoemission studies reported to date, are subject to various interpretations[3] and cannot be considered as proof of electronic configuration changes. In this Letter, we report the first definitive example of change in electronic configuration with particle size. This has been accomplished by measuring both core- and valence-level photoemission from Sm clusters on carbon supports.

Sm has several characteristics which make it uniquely suited for a study of this type. The free Sm atom is divalent $(4f^6)(sd)^2$, compared with the trivalent $(4f^5)(sd)^3$ state of the bulk metal. The divalent and trivalent configurations show a large core-level separation of 7.6 eV,[4] and the final-state $4f$ multiplet structures, $4f^5$ and $4f^4$, permit a clear distinction between the two possible initial-state configurations.[5-7] Furthermore, the divalent and trivalent states of Sm are known to be nearly degenerate[8,9] and coexist in intermedi-

ate-valence materials such as SmB_6,[6,10] and possibly even on the surface of Sm metal.[4-7,11]

We have performed both x-ray photoemission spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) of Sm clusters on amorphous carbon substrates. The XPS spectra were recorded on a UHV Hewlett-Packard spectrometer. The UPS spectra were recorded at 60-eV photon energy with a toroidal grating monochromator using synchrotron radiation from the Tantalus storage ring. This photon energy was chosen to maximize resolution and count rate. The clusters were prepared by vapor deposition onto amorphous carbon, cleaned by ion etching. Base pressures in both instruments were in the mid-10^{-11}- to low-10^{-10}-Torr region, rising to the low-10^{-9}-Torr region during deposition. Coverages were monitored by a quartz-crystal oscillator and checked by neutron activation analysis.

A strong coverage dependence of the electronic configuration is clearly seen in Fig. 1, which shows the Sm $3d_{3/2,5/2}$ spectra for various coverages including the bulk metal. The predominance of the 2+ species at low coverages is clearly observed and remains almost constant to a coverage of $(2-3) \times 10^{15}$ atoms cm^{-2}. Above this coverage region the 3+ intensity increases rapidly until a bulklike spectrum is achieved at about 1.2 $\times 10^{16}$ atoms cm^{-2}. The 3+/2+ intensity ratio is plotted graphically in Fig. 2 as a function of coverage.
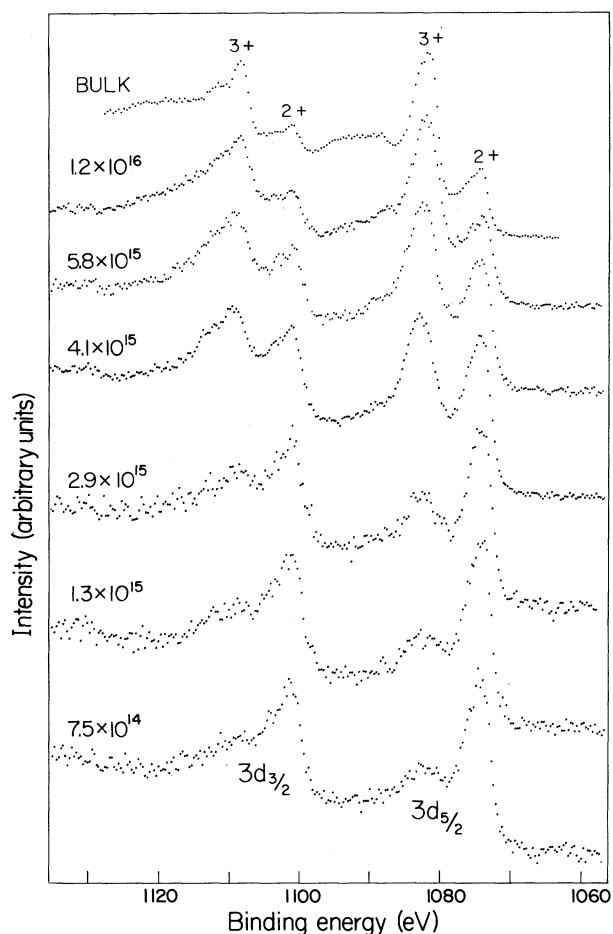
FIG. 1. Al $K\alpha$ x-ray photoemission spectra of the $3d$ region of carbon-supported samarium clusters at various coverages (atoms cm^{-2}).
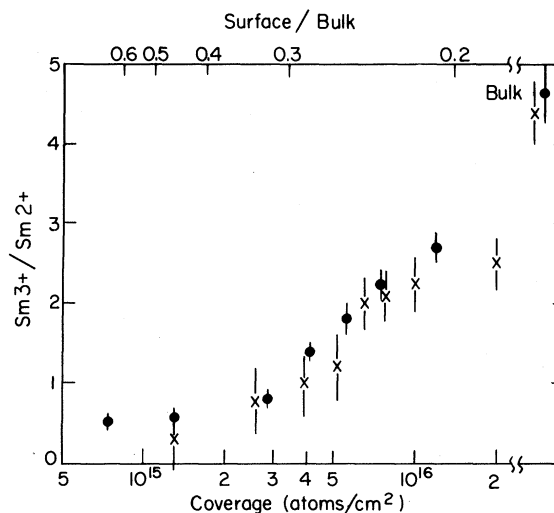

FIG. 2. Sm trivalent-divalent intensity ratio as a function of coverage and estimated surface-to-bulk atom ratio. XPS values (dots) were determined from $3d_{5/2}$ peak intensities, and UPS values (crosses) were determined from the peak C and A intensities. UPS data have been normalized to the XPS data at a coverage of 2.6×10^{15} atoms cm^{-2}.

The spectra measured at 60-eV photon energy are shown in Fig. 3 after subtraction of the carbon background. In these spectra, peaks C, D, and E are due to the $4f^4$ final-state multiplets produced by ionization of trivalent Sm.[6] Peaks A and B are primarily due to the $4f^5$ multiplets from divalent Sm with some contribution to A from $5d$ and $6s$ emission. The qualitative trends in valence spectra with coverage are very similar to those of the core $3d$ levels discussed above. The nearly identical variation in valence state with coverage is shown in Fig. 2. The UPS results are meant to be qualitative in regard to the absolute 3+/2+ ratio. The UPS data in Fig. 2 show the peak-C/peak-A intensity ratio which has been normalized to the XPS value at a coverage of 2.6×10^{15} atoms cm^{-2}. The close agreement between the two sets of data rules out the possibility that the 2+ peaks in XPS are low-binding-

energy satellites due to final-state screening effects[12] of the type observed weakly in some rare-earth metals.[13] This possibility seemed unlikely, even in the absence of the UPS results, because of the high intensity of the 2+ peak. On the contrary, one might postulate that the small 3+ contribution in the low-coverage XPS spectra is due to a $4f$-to-valence "shakeup" satellite. Some evidence for such a shakeup satellite appears in the $4d$ spectrum of metallic Eu.[14] An alternative explanation for the residual 3+ intensity is oxide formation resulting from oxygen contamination below our detection limits.

The possibility of the 2+ state resulting from the formation of a divalent carbide was also considered. Divalent samarium carbide can be made from the elements at high temperature (1400–1600 °C),[15] and its formation under the conditions used here cannot be ruled out a priori. We find no evidence for carbide formation such as changes in the C $1s$ spectrum. For comparison, in studies of reactive Al and Fe films the formation of a carbide is immediately obvious from the change in C $1s$ lineshape.[16] No such anomalies were observed in Sm clusters until the samples were heated to ~500 °C, at which time a weak shoulder appeared on the low-binding-energy side in the region characteristic of carbide carbon. Furthermore, it can be shown that changes in the
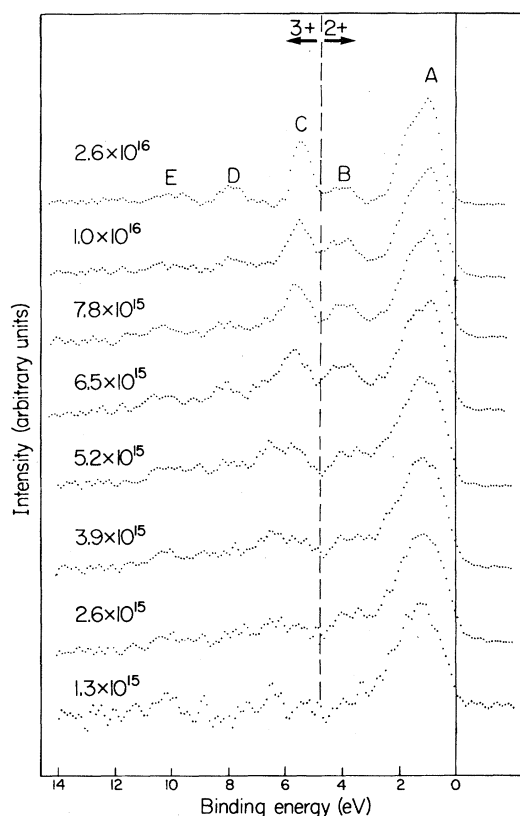
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FIG. 3. 60-eV photoemission difference spectra of the $4f$ and valence-band region of carbon-supported samarium clusters. Coverages are in atoms cm^{-2}, and the carbon background has been subtracted.

3+/2+ ratio shown in Fig. 2 are much too abrupt to result from carbide formation at the cluster-support interface. The observed slope must result from a collective effect such as a size-dependent electronic configuration.

It is clear from both the XPS and UPS spectra that Sm exists primarily in the divalent state at coverages below $(3-4) \times 10^{15}$ atoms cm^{-2}. From electron microscopy studies,[17] we estimate that a coverage of $\sim 2 \times 10^{15}$ atoms cm^{-2} corresponds to a mean particle size of 30 ± 10 Å. This also corresponds to the coverage range where the photoemission spectra of the noble and platinum-group metals begin to show bulklike characteristics.[2,18]

At higher coverages of $\sim 10^{16}$ atoms cm^{-2}, the clusters are no longer discrete but have coalesced to form a semicontinuous film with a very high surface-to-volume ratio. The approximate surface-to-bulk atom ratio is shown along the top of Fig. 2. The known stabilizing effect of a sur-

face for the divalent species causes the 3+/2+ ratio to remain below that of the bulk even at these high coverages where the transition and noble metals have achieved most of their bulklike properties. The stability of the divalent state in small clusters and on surfaces can be accounted for by a narrowing of the valence band as a result of reduced coordination. This raises the Fermi energy relative to the $4f$ levels and thus shifts a valence electron to populate the $4f^6(2+)$ state.[4]

The only previously reported studies of size-dependent configurations in rare earths were based on x-ray emission and bond-distance changes as determined by electron diffraction.[19] In the divalent metals Eu and Yb, a discontinuous lattice contraction at small sizes was taken to indicate a change from the 2+ to 3+ configuration. Surface tension was proposed as the mechanism for the lattice contraction, which raised the $4f$ levels relative to the Fermi level and caused a $4f$ electron to transfer to the conduction band. However, the vacuum conditions for these experiments were so poor that the results are highly questionable. Understandably, increased surface tension in small clusters favors the trivalent state. The competing factors of band broadening induced by surface tension and band narrowing as a result of reduced coordination will determine the actual electronic configuration for any specific small cluster. For samarium we have shown that band narrowing is the dominant effect, and thus the divalent state is dominant in these small clusters.

Changes in configuration with particle size should be a general feature of the rare-earth metals. All of the rare earths except cerium, gadolinium, and lutetium are divalent in the free atoms and except for europium and ytterbium are trivalent in the bulk metals. The remaining nine rare-earth elements must undergo a configuration change from 2+ to 3+ with increasing particle size. The size at which the changeover occurs is likely to depend upon the energy required to excite a conduction electron to the lowest empty $4f$ (Δ_+).[9] The transition is expected to occur at a larger particle size for those elements with a smaller Δ_+.

In summary, we have shown, for the first time, an unambiguous example of size-dependent electronic configurations. Both XPS and UPS spectra show a predominance of the atomiclike divalent state at small particle size. With increasing size, the bulklike 3+ state is formed, but a large divalent contribution from surface atoms re-

mains. These results may have significant impli-
cations for understanding the particle-size de-
pendence of demanding reactions in heterogene-
ous catalysis. In such systems involving transi-
tion-metal clusters we may reasonably expect
that electronic configurations will change in the
same size region as observed here for Sm.

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Probing the Electronic Structure of Metallic Glasses using Auger XVV Transitions

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The bandlike XVV Auger transitions of glass-forming elements are shown to pro-
vide a sensitive method for investigating the electronic properties of metallic glasses.
For amorphous $Fe_{82}B_{18-x}Be_x$, not only do the Auger results correlate remarkably
well with the magnetic data, but more importantly, a 14-eV shift was detected in the
Be KVV Auger spectra between $x = 4$ and $x = 5$. This large shift reflects a pronounced
change in the short-range order of this metallic glass system.

Attempts to understand the magnetic behavior
of iron-base metallic glasses in terms of satura-
tion magnetization (M_s), the average magnetic
moment per Fe atom ($\bar{\mu}_{Fe}$), and the Curie temper-
ature have been limited to magnetization meas-
urements supplemented by such experiments as
Mössbauer and NMR spectroscopies for indirect
information on related electronic properties. We
demonstrate in this Letter that the energy and
line shape of the Auger XVV (V is the valence