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Ultraviolet Photoelectron Spectra of Gallium Arsenide Clusters

by

C. Jin, K. J. Taylor, J. Conceicao, and R. E. Smalley

Chem. Phys. Letters (1990)

Rice University
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Houston, Texas

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ULTRAVIOLET PHOTOELECTRON SPECTRA OF GALLIUM ARSENIDE CLUSTERS

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ABSTRACT

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INTRODUCTION

Nearly five years ago in an initial supersonic cluster beam experiment with gallium arsenide clusters, O'Brien *et al.*[1] discovered a remarkable even/odd alternation in the ionization potentials (IP). Since the clusters were prepared by laser vaporization of a gallium arsenide disc in a high pressure pulsed supersonic nozzle, the clusters formed in a highly supersaturated vapor of gallium and arsenic atoms, and a wide range of Ga_xAs_y compositions were generated for every cluster size, n = x+y. Even so the remarkable observation was made that <u>all</u> even numbered clusters in the size range from 4 to 22 atoms had IPs higher than 6.4 eV, while the odd-numbered clusters with 5-21 atoms all had IPs less than 6.4 eV. Somewhat later Liu *et al.*[2] reported results from a crude bracketing of the thresholds for photodetachment of electrons from the negative cluster ions of Ga_xAs_y in the 2-30 atom size range, thereby providing rough estimates of the vertical electron affinity (EA). Again even/odd alternation appeared, with the odd-numbered clusters having the larger EA values.

Such even/odd alternation in IP and EA as a function of cluster size has been a common observation in single-valence- electron metal clusters such as Na,[3] K,[4] Cu,[5] Ag, and Au.[6] In these metal clusters the even/odd alternation arises because the atomic valence orbitals are strongly overlapping and for the small clusters a substantial gap exists between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). However, since these elements are all metallic in the bulk phase, it is perhaps not surprizing that this HOMO-LUMO gap soon becomes small enough that even/odd alternation in the IP and EA is no longer observed. In the case of gold clusters the even/odd alternation in IP and EA is extremely pronounced for clusters in the 2-20 atom size range, but it is largely gone by the time the cluster size is greater than 40.

Gallium arsenide, on the other hand, is potentially a far more complex situation than these simple group IA and IB metals. In bulk form it is a direct band gap semiconductor with a band gap of roughly 1.5 eV.[7] Cleavage of the surface along the (110) plane, for example, results in a surface with gallium or arsenic atoms each having a single sp^3 dangling bond. In the absence of relaxation this would leave a metallic surface density of states. However, relaxation does occur, leaving the surface gallium atoms with an unoccupied dangling bond, and the surface arsenic atoms with a dangling lone-pair. Such surface reorganizations effectively sweep the dangling bond states out of the gap in the surface density of states, producing a semiconducting surface.[8-10] Similarly effective relaxations or reconstructions are thought to occur on the other low miller index surfaces of GaAs.

In the case of small gallium arsenide clusters it is important to establish how effectively surface reconstruction can heal the dangling bonds. Particularly in the case encountered with supersonic beam sources which produce clusters with a wide range of compositions, the question of surface reconstruction appears at first to be impossibly complex. Yet the strong even/odd alternation in IP and EA for these clusters suggests that this reconstruction may be highly efficient. If so, it is possible that the even/odd alternation in IP and EA will continue through very large clusters, extrapolating to the bulk band gap. The ultraviolet photoelectron spectra

(UPS) survey experiments presented below were designed to test this hypothesis.

EXPERIMENTAL

Gallium arsenide clusters were prepared in a supersonic beam by laser vaporization of an undoped GaAs wafer. The pulsed supersonic cluster nozzle used in this work has been described in detail elsewhere.[6] Briefly, it involved the use of two fast pulsed valves of the magnetic "current loop" variety,[11,12] bolted to opposite sides of a 1.5 cm wide Teflon nozzle block. The opposing gas flows from these two valves (pulse duration 125 microsecond, 0.12 cm^3 atm flow per pulse) was synchronized to meet in a cylindrical "waiting room", 0.3 cm diameter, 1.0 cm long drilled into the center of the nozzle block. The rotating, translating GaAs target disc was mounted on the back of this block, and the Nd:YAG 2nd harmonic vaporization laser beam (10-15 mJ $pulse^{-1}$, 5 nsec duration) was directed down the axis of the supersonic beam apparatus through the cylindrical waiting room, and focussed to a 0.1 cm diameter spot on the GaAs target disc. Cluster ions formed from the vaporized GaAs plasma in the waiting room accelerated with the helium carrier gas through a 0.2 cm diameter orifice, and passed through a 6 cm long nozzle cone, 10^0 internal angle. The resulting supersonic jet was then skimmed by a conical skimmer 15 cm downstream from the exit of the nozzle cone. The negatively charged $Ga_xAs_y^-$ clusters were then pulsed out of the beam with a tilted extraction stack[13] operating at 1000 Volts, and directed the cluster ion beam into the magnetically-focussed time-of-flight UPS apparatus discussed in previous publications from this group.[5,6,14] An F_2 excimer laser (photon energy 7.9 eV) was used for photodetachment of the mass-selected $Ga_xAs_y^-$ clusters.

In earlier studies of Ga_xAs_y clusters in this group it was noted that the clusters tended to lose arsenic (probably in the form of As_2 and As_4) when heated.[1,2,15] When the laser vaporization cluster nozzle is operated to yield a substantial number of cluster ions derived from the original laser-induced plasma ionization, much of the cluster growth occurs while the buffer gas temperature is rather high. In the case of GaAs this often produces Ga_xAs_y clusters for which the x:y composition distribution is peaked somewhat to the gallium rich side (x>y).[15] For this reason we optimized the operation of the cluster nozzle to minimize this arsenic loss as much as possible. Nonetheless, it was clear from careful calibration of the mass spectra of the $Ga_xAs_y^-$ cluster beams used in this study that the distributions were skewed to the gallium-rich side, the maximum occurring near the composition with y=x+2.

The UPS apparatus was calibrated by measurement of the spectrum of Au^- and using the published values for the EA,[16] and the first few excited electronic states of the neutral atom.[17] In this UPS apparatus the effective photoelectron resolution is dependent on the translational velocity of the cluster ions at the moment of photodetachment.[5] For the clusters with less than 20 atoms we decelerated the negative cluster ion beam to the range of 100-200 eV. Above 20 atoms this velocity effect on the resolution was small enough that deceleration from the original 900 eV energy of the pulse extracted $Ga_xAs_y^-$ beam was unnecessary. The effective resolution of the UPS apparatus for the data reported below was 0.05 to 0.1 eV. All the spectra reported below were recorded as the accumulation of data from 10^4 pulses of the cluster beam apparatus with background photoelectrons subtracted on

alternate laser shots. The resultant photoelectron spectra were smoothed with a 0.05 eV square window function.

RESULTS AND DISCUSSION

Figures 1-3 present the recorded UPS spectra of mass-selected $Ga_xAs_y^-$ clusters in the size range x+y = 2 through 50. With the exception of the UPS data for the two atom cluster (which refers to the $GaAs^-$ diatomic), our mass resolution was insufficient to pick out a single x,y composition. For the larger clusters, even with orders of magnitude higher mass resolution it would have been impossible to select purely a single x,y composition from the Ga_xAs_y clusters due to the overlapping mass distributions caused by the ^{69}Ga and ^{71}Ga isotopes of gallium in natural abundance. Instead we timed the firing of the photodetachment laser to intersect the section of the cluster time-of-flight spectrum corresponding to the time calculated for the stoichiometric 1:1 composition. For the even numbered clusters we chose the photodetachment time appropriate to the x=y composition of the mass-selected $Ga_xAs_y^-$ clusters, for the odd numbered clusters we chose the time calculated for the x=y+1 cluster. It is therefore important in interpreting these spectra to realize that they pertain to a range of cluster compositions, and also most certainly to a range of isomeric structures for each of these compositions as well.

One of the virtues of photoelectron spectroscopy of the negative ions is that the photodetachment threshold provides a direct measure of the vertical electron affinity. In order to estimate the detachment thresholds on such a broad range of poorly resolved spectra we adopted the following simple approach. For each spectrum a straight line fit was made to the rising slope of the first significant spectral feature. The vertical electron affinity was then taken to be the baseline intercept of this straight line plus a constant offset of 0.35 eV as a crude correction for cluster temperature and instrument resolution effects. These EA estimates are tabulated in Table I, and plotted in Figure 4.

As expected from earlier work with GaAs negative clusters,[2] even/odd alternation is evident in the EA as a function of cluster size. Although there can certainly be some disagreement with our way of picking the thresholds, we believe any reasonable method will result in the same conclusion: the even/odd alternation in the vertical EA is strong, and this alternation persists without substantial narrowing at least through 50 atoms.

In the earlier photodetachment work of Liu *et al.*[2] some evidence was presented indicating that the EAs tended to decrease for a given cluster size as one examined Ga_xAs_y clusters with compositions of decreasing x/y ratio. With the current UPS work this effect was quite evident when spectra were taken from differing regions of the composition-broadened mass peaks for any particular cluster size. For example, Figure 5 shows the UPS patterns obtained for the 23 atom cluster at the masses approximately corresponding to (x,y) composition values of (18,5), (12,11), and (5,18), respectively. The variation in apparent vertical EA for these clusters is nearly 0.5 eV. As listed in Table 1, similar results were obtained from spot checks of the composition variation of EA were made for a number of clusters. Although this variation in EA across compositions for a single cluster size is within a factor of two as large as the observed even/odd variation between different cluster sizes, it was always found to be monotonic, and the even/odd

alternation in EA was always evident as long a clusters of similar x/y composition ratios were compared.

For the small cluster in the 2-6 atom size range the mass resolution and isotopomer distributions are sufficiently narrow in the experiment to obtain highly structured UPS patterns for individual compositions. The spectrum shown in Fig. 1 for the diatomic is an example -- it is from the $GaAs^-$ molecule. In accord with the assignment of the optical spectrum of the neutral molecule,[18] and recent theoretical calculations,[19-20] this UPS pattern shows that GaAs has an open-shell triplet ground state with an EA which is actually higher than the next odd-numbered cluster. Of all the even-numbered Ga_xAs_y clusters we have studied, this diatomic is the sole exception to the rule of uniform even/odd alternation in the EA as a function of cluster size. Detailed analysis of these small Ga_xAs_y cluster UPS patterns will be reserved for a latter paper. High resolution study of such spectra should provide direct tests of theoretical calculations for these species.

SUMMARY

The UPS patterns of mass-selected $Ga_xAs_y^-$ clusters near the x=y composition reveals an even/odd alternation in vertical electron affinity that persists without significant narrowing through clusters 50 atoms in size. Together with the corresponding odd/even alternation in ionization potentials discovered earlier,[1] these new EA data strongly support the notion that relaxation/reconstruction of the surface of these GaAs clusters is highly facile. With the sole exception of the GaAs dimer, all the even-numbered clusters appear to have closed-shell ground state singlet states (for the neutral clusters) with substantial HOMO-LUMO gaps. The odd-numbered clusters will of course be open shell species as neutrals simply by virtue of the fact that they have an odd number of electrons, but the observed alternation in the IP of the neutral clusters shows that the HOMO for the odd-numbered clusters is always less tightly bound than for the even-numbered clusters. Preliminary results from extended Huckel and local spin density calculations currently underway in this laboratory on gallium arsenide clusters in the 2-20 atom size range are in agreement with this interpretation.[21] The unfilled HOMO of odd-numbered clusters tends to be a largely non-bonding molecular orbital with an energy slightly less than half the HOMO-LUMO gap of the adjacent even-numbered clusters of the same x/y compositon. If this trend continues through large clusters, the EA of the even-numbered clusters should asymptotically approach the 4.07 eV electron affinity of the perfect bulk crystal, while the EA of the odd-numbered clusters should evolve to a value slightly below 4.8 eV (the bulk EA plus half the intrinsic band gap).

As was evident even in the rough EA bracketing results of Liu *et al.*[2] the electron affinity of gallium arsenide clusters plotted in Fig. 4 approaches the bulk value of 4.07 eV[7] much more rapidly than is typical with simple metal clusters such as potassium[4] or copper[5]. This is another indication that these small clusters are behaving as semiconductors. Since the screening length for semiconductors such as GaAs is much longer than the radius of clusters in the 2-100 atom size range, screening is far less important here than with metal clusters. Furthermore, any semiclassical model based on uniform charging of a sphere[22] is unlikely to be effective for these semiconductor cluster ions since the extra charge is apt to be concentrated near a few surface corner atoms. For even the most perfect possible macroscopic GaAs crystal the corners between otherwise perfectly reconstructed

surface facets will act as shallow traps slightly below the bottom of the bulk conduction band. These corner traps are likely sites for localization of the excess charge of the negative ion. To the extent the charge is localized, it will not take a very large cluster to mimic this effect. For a variety of reasons, therefore, these small nanometer-scale clusters may be quite adequate models of much of the physics and chemistry that occurs on the surface of bulk gallium arsenide.

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FIGURE CAPTIONS

FIGURE 1. Photoelectron spectra of mass-selected $Ga_xAs_y^-$ clusters near the composition x=y as a function of cluster size, n = x+y, in the range n=2-19 atoms. The spectra were recorded using a F_2 excimer photodetachment laser (photon energy 7.9 eV).

FIGURE 2. Photoelectron spectra of mass-selected $Ga_xAs_y^-$ clusters in the 20-37 atom size range.

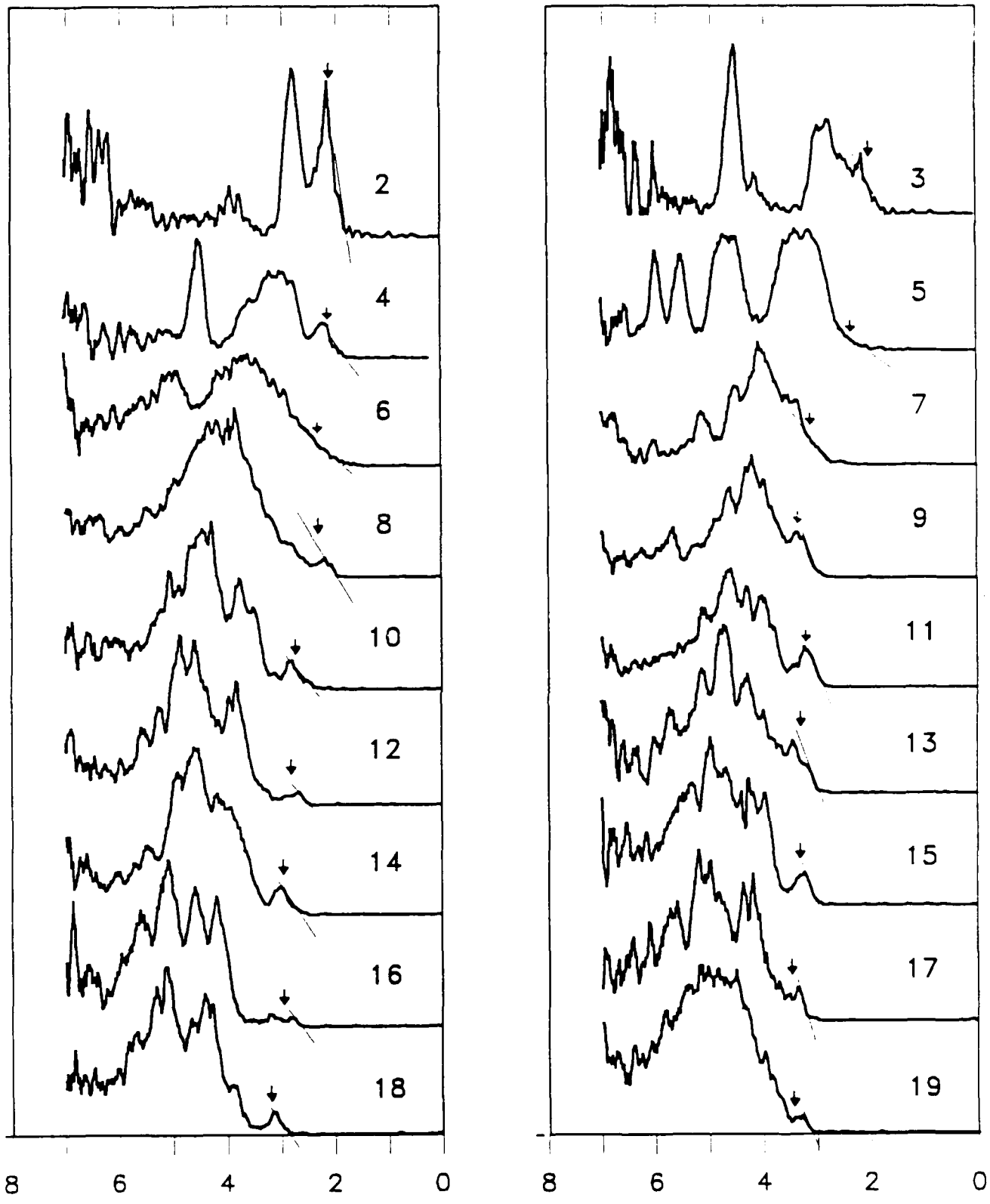
FIGURE 3. Photoelectron spectra of mass-selected $Ga_xAs_y^-$ clusters in the 38-50 atom size range.

FIGURE 4. Vertical electron affinity of Ga_xAs_y clusters near the x=y composition as estimated from photoelectron spectra of the mass-selected negative cluster ions.

FIGURE 5. Photoelectron spectra of 23 atom $Ga_xAs_y^-$ clusters at the masses approximately corresponding to (x,y) compositions of (18,5), (12,11) and (5,18), respectively.

TABLE I. Estimated vertical electron affinities of $Ga_xAs_y^-$ clusters as a function of cluster size, n = x+y.

Cluster size	EA (eV)	Cluster size	EA (eV)	Cluster size	EA (eV)
2	2.1	19	3.4	36	3.7
3	1.9	20	3.1	37	4.3
4	2.1	21	3.5	38	3.6
5	2.3	22	3.2	39	4.3
6	2.1	23	3.8	40	3.7
7	3.1	24	3.4	41	4.3
8	2.3	25	4.0	42	3.9
9	3.3	26	3.4	43	4.3
10	2.7	27	3.9	44	3.9
11	3.2	28	3.4	45	4.3
12	2.8	29	4.0	46	3.8
13	3.3	30	3.6	47	4.2
14	2.9	31	4.1	48	4.0
15	3.3	32	3.6	49	4.2
16	2.9	33	4.1	50	3.9
17	3.5	34	3.6		
18	3.2	35	4.2		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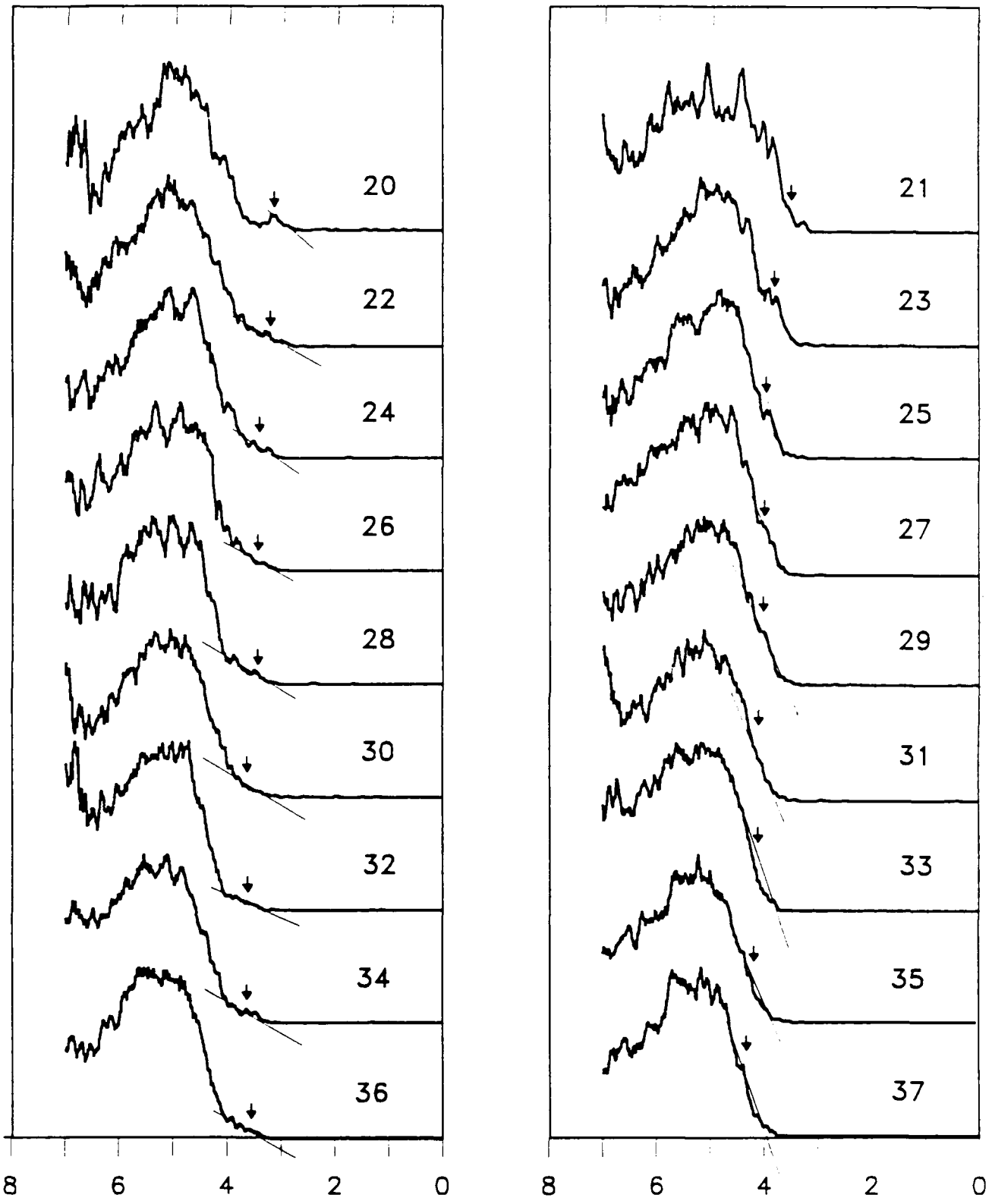
BINDING ENERGY (eV)

Fig. 1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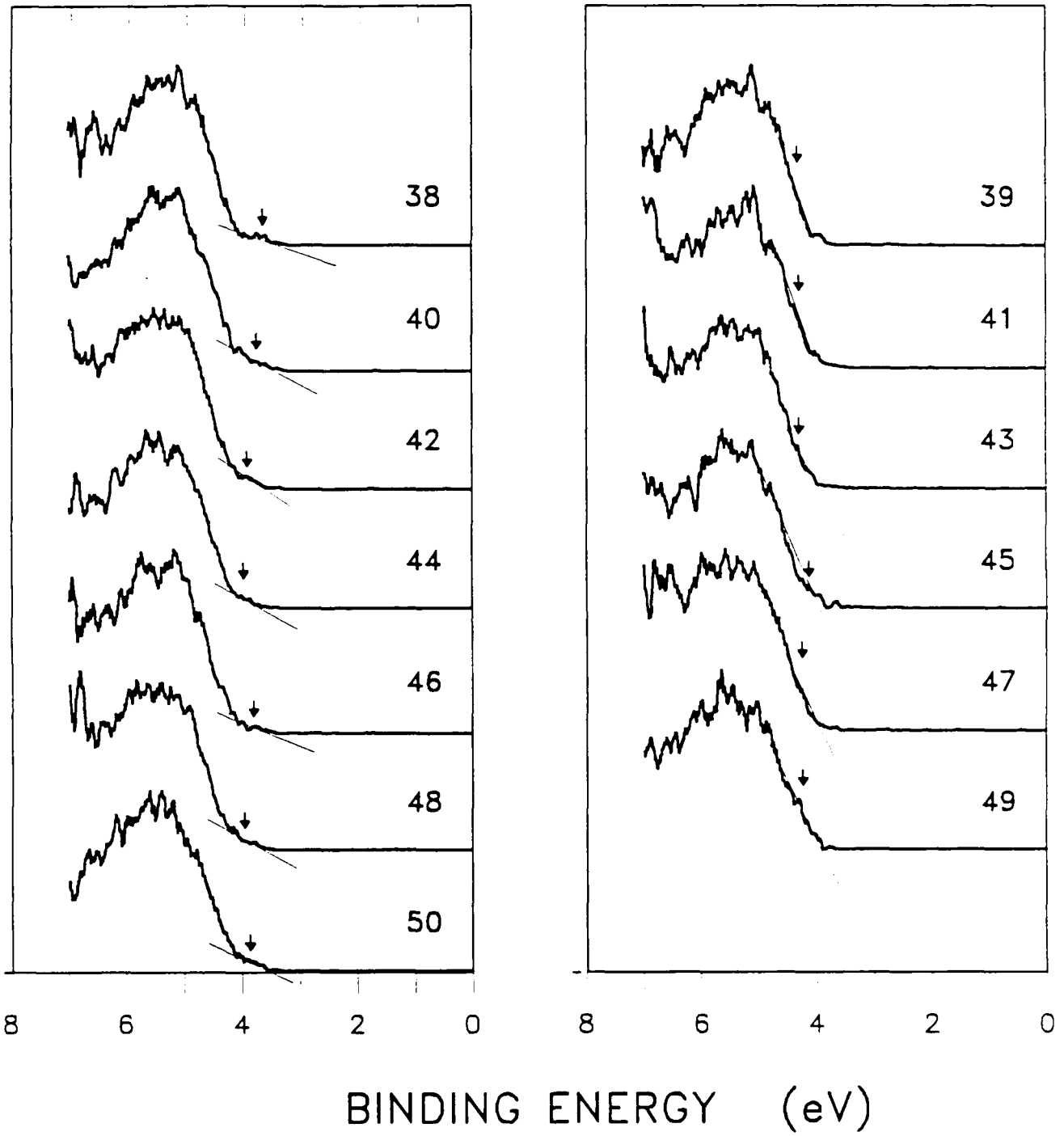
BINDING ENERGY (eV)

Fig. 2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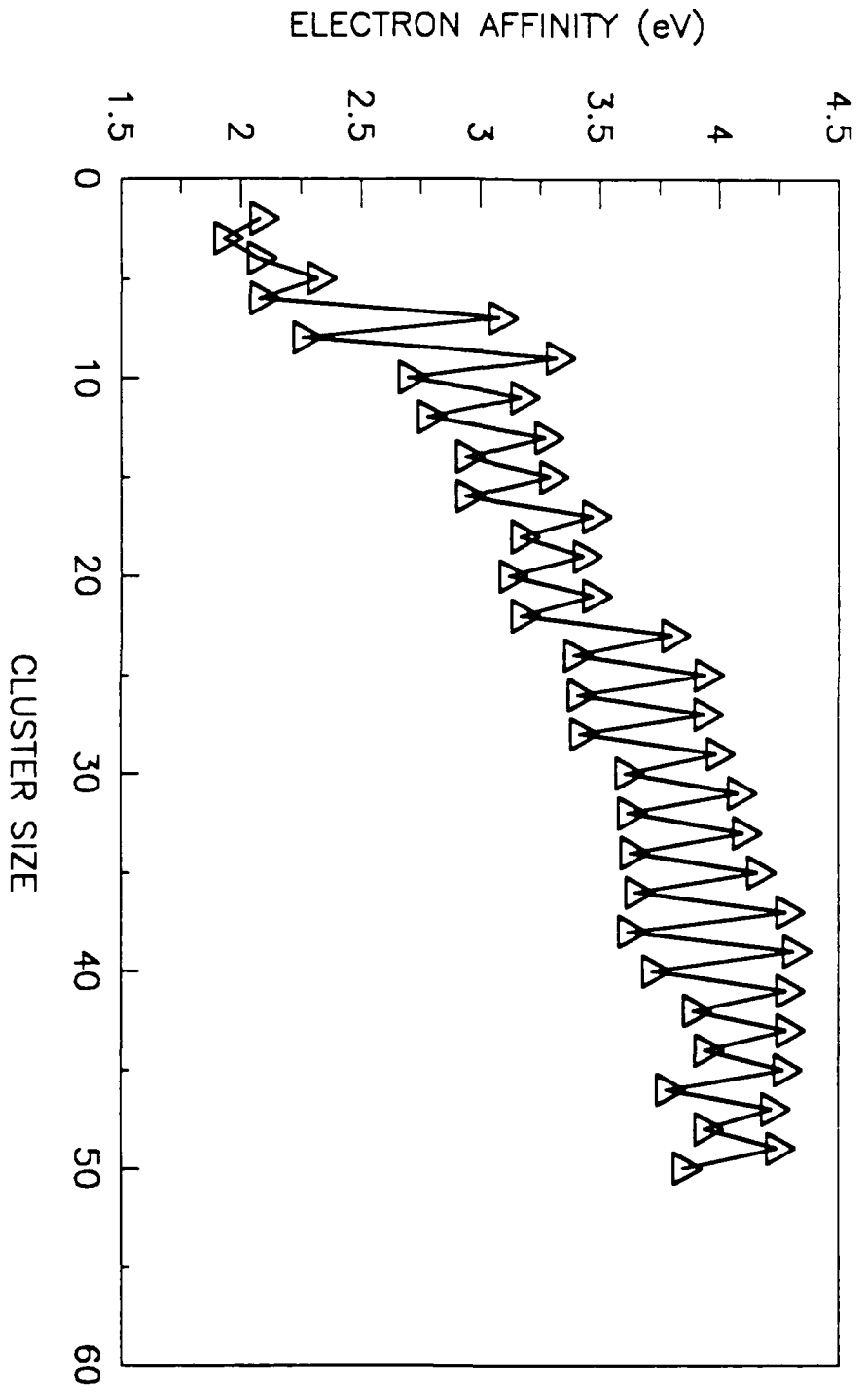
BINDING ENERGY (eV)

Fig. 3


ELECTRON AFFINITY (eV)
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3.5
4
4.5
0
10
20
30
40
50
60
CLUSTER SIZE

Fig. 4

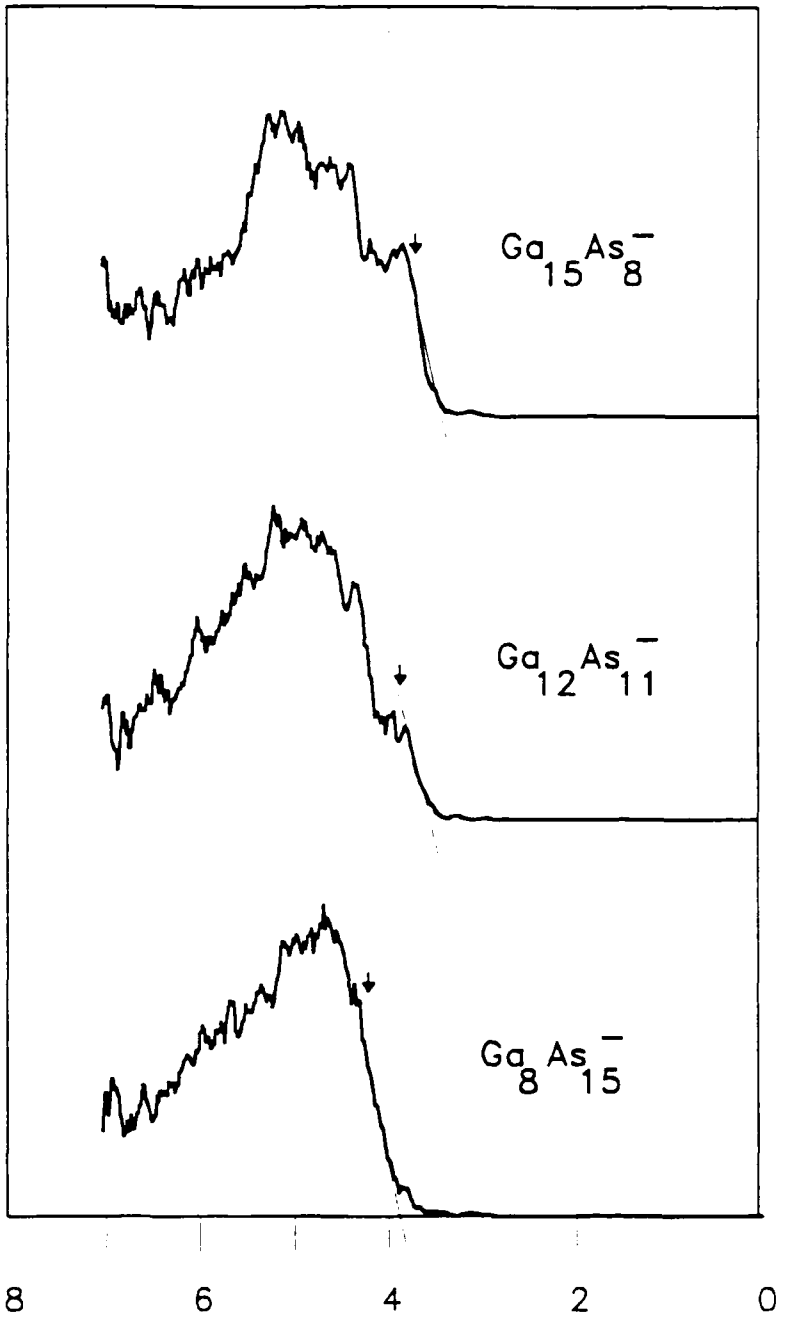

Fig. 5