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Evolution of electronic structure as a function of size in gallium phosphide semiconductor clusters

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Abstract

Anion photoelectron spectra have been taken of $Ga_xP_y^-$ clusters at a photodetachment wavelength of 266 nm (4.657 eV). Clusters of varying stoichiometry with up to 18 atoms have been investigated. We obtain electron affinities and vertical detachment energies to the ground and low-lying excited states of the neutral clusters. Photoelectron spectra of clusters with 3–5 atoms are compared to previously reported ab initio calculations. Trends in the electron affinities and excitation energies for the larger clusters are discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Understanding the spectroscopic and thermodynamic properties of semiconducting particles as a function of size has become increasingly important in the search for technological advances in the fabrication of smaller and faster electronic devices. This has motivated the study of semiconductors in several size regimes. Semiconductor nanocrystals, particles typically in the size range of 10^3 or more atoms, have been the focus of much research in recent years [1–6]. The spectroscopy of these species, particularly quantum confinement effects, can generally be understood in terms of perturbations to the macroscopic material related to their finite size. Molecular clusters in the range of 10–100 atoms present additional challenges, as they are generally too small to be considered as perturbed macroscopic material but too large to treat with the standard spectroscopic and theoretical methods that work so well for small molecules. It is therefore of considerable interest to determine how the structure and spectroscopy of molecular clusters evolve with size. In this Letter we address this issue for gallium phosphide clusters by photoelectron spectroscopy of size-selected cluster anions of various stoichiometries with up to 18 atoms.

Photoelectron spectroscopy of anions has been an important tool for studying size-dependent properties of clusters, as it combines mass-selectivity with moderate spectral resolution. The photoelectron spectra of homonuclear semiconductor clusters such as Si_n^- [7–11] and Ge_n^- [8,12] are well-characterized. Heteronuclear clusters present additional complexity since both size and stoichiometry can be varied. The first systematic study of heteronuclear semiconductor clusters was performed on $Ga_xAs_y^-$ clusters by

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Smalley and co-workers [13,14]. Wang et al. [15] and Kaya and co-workers [11] have measured photoelectron spectra of $Si_xO_y^-$ and $Si_xC_y^-$ clusters, respectively.

We have previously reported photoelectron and zero electron kinetic energy (ZEKE) spectra of small $In_xP_y^-$ clusters ($x, y \leq 4$) [16,17]. This work and the photodissociation studies by Kolenbrander and Mandich [18] on neutral InP clusters have shown that the spacing between the ground and first excited electronic states in the neutral clusters was close to the bulk InP band gap of 1.344 eV (300 K). InP is a direct gap semiconductor, while GaP has an indirect band gap of 2.272 eV (300 K). If these significant differences in the bulk electronic structure are reflected in the molecular cluster size regime, one would expect rather different photoelectron spectra for small GaP and InP clusters; this was a major motivation for the work presented here. More generally, we wish to compare our results to previous experimental and theoretical investigations in the hope of understanding the electronic structure of these clusters and how they extrapolate to the bulk properties.

Only four experimental studies of gallium phosphide clusters in any size range have been published. Nozik and co-workers [19] have taken the optical absorption spectra of passivated nanocrystals in the 20–30 Å size regime. Stucky and co-workers [20] measured spectra of GaP clusters in a similar size range produced in the cavities of zeolite Y. Both observed quantum confinement effects, but found that the optical spectra anomalously extended to the red of the indirect gap in bulk GaP. In the small molecule regime, Weltner and co-workers [21] have recorded the IR absorption spectrum of GaP, Ga_2P, and GaP_2 trapped in a 4 K argon matrix. From these spectra they were able to obtain isotope specific vibrational fundamentals for these species. Huang et al. [22] have measured mass spectra of GaP cluster anions produced by laser ablation and observed a tendency for the clusters to have more gallium than phosphorus atoms.

Theoretical investigations of GaP clusters have been carried out by Andreoni [23], Ramakrishna and co-workers [24,25], and Feng and Balasubramanian [26–29]. Andreoni used the Car–Parrinello molecular dynamics method to study the structures, stability, and melting of small stoichiometric GaAs, GaP, and AlAs clusters. Ramakrishna and co-workers have used an empirical pseudopotential method to investigate the electronic states of GaP nanocrystals ranging from 5–100 Å in radius. These calculations predict the nanocrystals to change from an indirect to a direct band gap semiconductor for clusters smaller than ~20 Å, a prediction which has yet to be confirmed experimentally. Feng and Balasubramanian have performed ab initio calculations on a series of Ga_xP_y clusters with five or fewer atoms [26–29]. They calculated ground and excited state geometries and energies at the complete active space self-consistent field (CASSCF) and multi-reference singles-doubles configuration interaction (MRSDCI) levels of theory.

The spectra reported here represent the first study of the electronic structure of gallium phosphide in the molecular cluster size regime. We obtain electron affinities (EAs) and vertical detachment energies (VDEs) to the ground and low-lying electronic states of the neutral clusters. In general, the photoelectron spectra of $Ga_xP_y^-$ clusters are quite similar to those of $In_xP_y^-$ clusters [17,30]. Photoelectron spectra of the smallest clusters can be directly compared to the ab initio calculations of Feng and Balasubramanian in order to assign the observed electronic transitions. Trends in the larger clusters are also discussed; the most notable of these is that the EAs of stoichiometric ($x = y$) clusters with 10 or more atoms appear to extrapolate smoothly to the bulk value.

2. Experimental

The anion photoelectron spectrometer used in this study has been described in detail previously [31,32]. Cluster anions were generated in a laser ablation/pulsed molecular beam source. A rotating and translating single crystal disc of GaP (Crystallode) was ablated with second harmonic (532 nm) of a pulsed Nd:YAG laser. The laser pulses were typically 5.0–7.5 mJ pulse^{-1} before focussing on the target with a 1 m lens. Any ablated material is caught up in a supersonic beam of argon expanded through a pulsed piezoelectric valve at a backing pressure of 20 psig. The negative ions pass through a skimmer into a differentially pumped region. They are extracted perpendicular to their flow direction by a pulsed electric field and injected into a linear reflectron time-of-flight (TOF) mass spectrometer [33,34], affording a mass resolution $m/\Delta m$ of 2000. The ions of interest are selectively photodetached with the fourth harmonic of a pulsed Nd:YAG laser(266 nm, $h\nu = 4.657$ eV). The electron kinetic energy (eKE) distribution is determined by TOF analysis in a field-free flight tube. For these experiments an electron flight tube length of 30 cm was used in order to increase the signal collection over our previous 100 cm long flight tube. The energy resolution is 30 meV at 0.65 eKE and degrades as $(\mathrm{eKE})^{3/2}$ at higher eKE. The laser polarization can be rotated by means of a half-wave plate. Secondary electrons initiated by scattered photons necessitate the collection and subtraction of background spectra in the spectra taken at high laser power.

3. Results

Fig. 1 shows the mass spectrum of $\mathrm{Ga}_x\mathrm{P}_y^-$ cluster anions produced by the laser ablation source; it represents a composite of three different mass spectra, each taken under different source conditions to optimize a particular mass range. The spectrum is composed of bunches of peaks separated in mass by a Ga atom. Each bunch of peaks is composed of 2–3 different cluster stoichiometries, as shown in the inset. Each cluster stoichiometry is represented by several peaks due to the natural isotope abundance of gallium (Ga^{69}:Ga^{71}, 100.0:66.4) which increases the complexity of the spectrum as the number of Ga atoms increases. The stoichiometries and intensities of the clusters are very sensitive to the laser power and the angle at which the laser beam impinges the disc. Although the ion intensities are very dependent on the source conditions, all of the mass spectra show that the most intense peaks are always of the stoichiometry, $\mathrm{Ga}_x\mathrm{P}_{1-4}$. In general higher laser ablation pulse energies produce more Ga-rich clusters.

The masses that were photodetached are marked with an asterisk. The mass value and the stoichiometry of each cluster can be found in Table 1. The most intense peak in the isotope distribution was always detached for any given cluster stoichiometry. The stoichiometric $(x = y)$ clusters $\mathrm{Ga}_1\mathrm{P}_1$, $\mathrm{Ga}_8\mathrm{P}_8$, $\mathrm{Ga}_9\mathrm{P}_7$, and $\mathrm{Ga}_9\mathrm{P}_9$ are not marked in the figure due to their very low intensity.

Figs. 2 and 3 show 35 photoelectron spectra of $\mathrm{Ga}_x\mathrm{P}_y^-$ taken at a photon energy of 4.657 eV. In

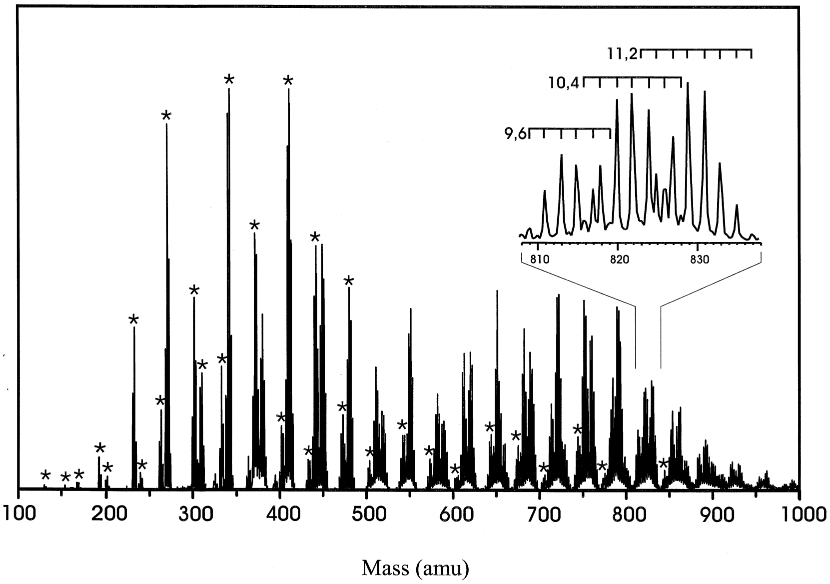

Fig. 1. Mass spectrum of $\mathrm{Ga}_x\mathrm{P}_y^-$ clusters. This is a composite of three spectra obtained under different source conditions. Asterisks ($*$) mark the peaks that were photodetached. The inset shows the individual mass peaks comprising the bunch around 820 amu.

Table 1
Estimated adiabatic electron affinities and vertical detachment energies for $Ga_xP_y^-$

Cluster Ga, P	Mass (amu)	Adiabatic EA (eV)	Vertical detachment energy, VDE (eV)				
			X	A	B	C	D
1, 1[a]	100	1.96	2.11	2.20	2.72	3.66	
1, 2[a]	131	1.78	1.98	2.97	4.32		
1, 3[a]	162	1.95	2.19	2.57	3.65	4.30	
1, 4[a]	193	3.48	3.80	4.03			
2, 1[a]	171	2.42	2.50	2.77			
2, 2[a]	202	1.86	2.08	2.98	3.93	4.66	
2, 3[a]	233	3.03	3.14	3.35	4.66		
2, 4[a]	264	2.40	2.67	3.48	4.27		
3, 1[a]	240	1.88	1.93	2.89	3.34		
3, 2[a]	271	3.03	3.27				
3, 3[a]	302	2.50	2.67	3.04	3.39	3.91	4.35
3, 4[a]	333	3.12	3.23	3.46	4.40		
4, 1[a]	309	2.09	2.20	3.16	3.29	3.87	
4, 2[a]	340	2.16	2.29	3.27	3.58		
4, 3[a]	371	2.88	3.28	3.75			
4, 4	402	2.33	2.59	3.42	4.10		
4, 5	433	2.47	3.52	3.86			
5, 2[a]	411	2.37	2.48	3.37	3.68	4.04	
5, 3	442	2.67	3.42				
5, 4	473	3.11	3.28	4.03	4.48		
5, 5[a]	504	2.81	2.93	3.80	4.42		
5, 6	535	3.27					
6, 3[a]	511	3.05	3.22	3.53	4.03		
6, 4	542	2.83	2.93	3.86	4.14		
6, 5	573	2.97	3.32	3.72	4.35		
6, 6	604	2.74	2.93	3.27	4.03	4.46	
7, 5[a]	644	2.95	2.96	3.60	4.39		
7, 6	675	3.39	3.48	4.50			
7, 7	706	2.81	2.93	4.40			
8, 6	744	3.11	4.38				
8, 7	775	3.33	4.46				
8, 8	806	3.04	3.13	4.32			
9, 7	844	3.00	3.23				
9, 8	875	2.97	3.21				
9, 9	906	2.92					

[a] These EAs have and uncertainty of ±75 meV. All others are ±150 meV.

these spectra the electron kinetic energy, eKE, is related to the internal energy of the neutral and anion by the following equation, $\mathrm{eKE} = h\nu - \mathrm{EA} - E^0 + E^-$. Here, $h\nu$ is the photon energy, EA is the adiabatic electron affinity, E^0 is the internal energy of the neutral, and E^- is the internal energy of the anion. The spectra show peaks corresponding to different electronic states of the neutral cluster, with the lowest-lying state occurring at the highest eKE. The only state for which vibrational structure is resolved is at lowest eKE in the GaP_2^- spectrum. All of the spectra shown in Fig. 2 were taken at a laser polarization of $\theta = 55°$, the 'magic angle', with respect to the electron detector; we obtained spectra at other laser polarization angles for selected clusters but observed little or no effect on the peak intensities.

Photoelectron spectra of the stoichiometric clusters Ga_1P_1–Ga_9P_9, Ga_9P_7, and Ga_9P_8 were taken at a laser fluence of 2.5 mJ cm^{-2} $pulse^{-1}$. Spectra of the other clusters were taken at a fluence ten times higher, and many of these show a common feature marked with an asterisk. The absence of this feature at lower laser fluence suggests that it results from a two-photon process involving photodissociation and subsequent photodetachment of a common daughter ion, and we do not consider it further in the assignments discussed below.

The spectra directly yield VDEs for each neutral electronic state, using $\mathrm{VDE} = h\nu - \mathrm{eKE}_{\max}$, where $\mathrm{eKE}_{\max}$ is the electron kinetic energy at the band maximum for the state in question. Where possible, these maxima are marked by dots in Fig. 1, and the corresponding VDEs are given in Table 1. For each cluster, the peaks are labeled X, A, B, C, etc., in order of increasing VDE. The adiabatic EA, i.e. the energy needed to form the ground electronic and vibrational state of the neutral from the anion ground state, is also of interest. Determination of the EA is complicated by absence of vibrational structure. The arrows in each spectrum indicate our best estimate of the ground state origins; these are generally taken to lie at the point of inflection at highest eKE. The resulting EAs are tabulated in Table 1.

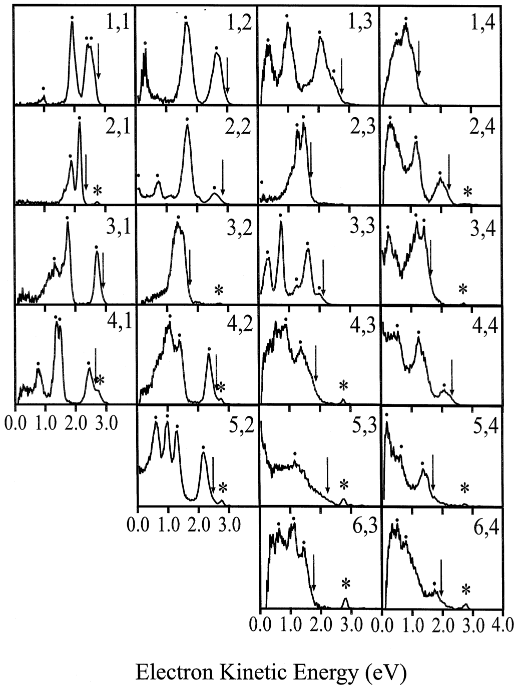

Fig. 2. Photoelectron spectra of the smaller $Ga_xP_y^-$ clusters taken at 266 nm (4.657 eV). All spectra were taken at a laser polarization of $\theta = 54.7°$ with respect to the direction of electron collection.

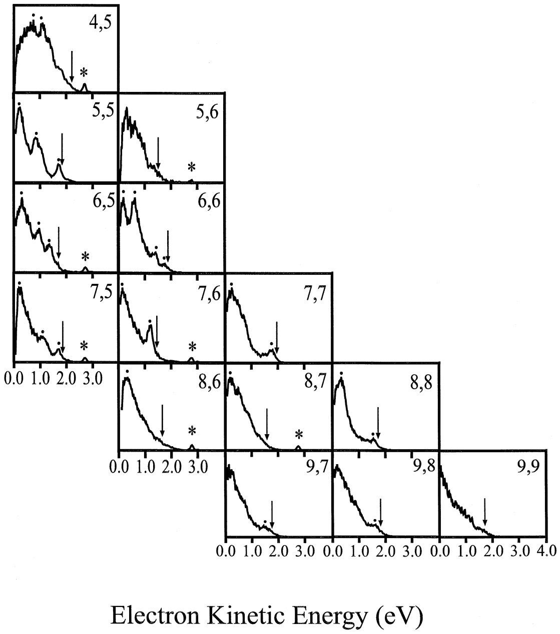

Fig. 3. Photoelectron spectra of the larger $Ga_xP_y^-$ clusters taken at 266 nm (4.657 eV). All spectra were taken at a laser polarization of $\theta = 54.7°$ with respect to the direction of electron collection.

4. Smaller clusters

Assignment of electronic features in the gallium phosphide photoelectron spectra for clusters with 3–5 atoms is possible through comparison with the calculations of Feng and Balasubramanian at the CASSCF and MRSDCI levels of theory. For GaP_2 Feng and Balasubramanian find a $^2B_2$ ground state with C_{2v} symmetry and a ∠P–Ga–P bond angle of 43.9°, indicating strong P–P bonding. The low-lying $^2A_1$ and $^2B_1$ excited states, also with C_{2v} symmetry, are predicted to have term energies of 1.07 and 2.33

eV, respectively, and considerably larger bond angles of 56.0 and 55.8°, respectively. In the GaP_2^- photoelectron spectrum, the difference in the VDEs for peaks X and A is 0.99 eV, and that for peaks X and B is 2.34 eV. Based on the agreement with theory, we assign peaks X, A, and B to transitions to the $^2B_2$, $^2A_1$, and $^2B_1$ states of GaP_2. Higher-resolution studies of this and other small GaP clusters are currently in progress, and a discussion of the vibrational structure in peak B will be deferred until this work is complete.

Ga_2P is calculated to have a $^2B_1$ electronic ground state (C_{2v}) with a bond angle of 111°. In our photoelectron spectrum the transition to the ground state is narrow (100 meV FWHM) and intense, indicating very similar geometries in the neutral and anion, in particular that the anion is also strongly bent. Peak A is also a relatively sharp feature, indicating that Ga_2P is bent in this electronic state as well. It is located 0.27 eV above the ground state as calculated by the difference in VDEs. In Feng and Balasubramanian's calculation the next excited state, the $^2B_2$ state, lies 0.09 eV above the ground state with a bond angle of 93°. Two additional linear states, the $^2\Pi_u$ and $^2\Sigma_u$ states, are calculated to lie 0.16 and 0.34 eV above the ground state. While any of these three excited states is a candidate for peak A based on energies alone, detachment to the two linear states would yield very extended progressions, rather than the sharp peak A seen in our spectrum. Therefore we assign peak A to the $^2B_2$ state.

The $Ga_2P_2^-$ photoelectron spectrum shows four distinct peaks, with peak A considerably more intense than the other three. Peaks X and A have similar widths, while peak B is narrower. Based on differences in the VDEs, peaks X and A are separated by 0.90 eV, while peaks X and B are separated by 1.85 eV. These results can be compared to ab initio calculations on Ga_2P_2, which is predicted to be a rhombus having D_{2h} symmetry with a closed-shell ^1A_g ground state. At the MRSDCI level of theory, the lowest-lying excited states and their energies are ^3A_u (1.182 eV), ^1A_u (1.376 eV), $^3B_{2g}$ (1.527 eV), and $^1B_{2g}$ (1.789 eV). The leading configuration of the ^1A_g ground state is $\ldots 1b_{2u}{}^2\, 1b_{1u}{}^2\, 2b_{1u}{}^2\, 1b_{3g}{}^2$-$1b_{3u}{}^2\, 1b_{1g}^0$ so , assuming the anion is formed by addition of an electron to the $1b_{1g}$ orbital, all of these excited states are accessible via one-electron detachment. Our previous study of Si_4^- showed that transitions to triplet and singlet open-shell states with the same molecular orbital configuration (e.g., the ^3A_u and ^1A_u states) should have similar intensities. The assignment most consistent with the calculations is that peak A is an overlapping transition to the ^3A_u and ^1A_u states, and that peaks B and C are transitions to the $^3B_{2g}$ and $^1B_{2g}$ states, respectively. This assignment is somewhat problematic as it implies the $^3A_u/^1A_u$ splitting is smaller than calculated, while the $^3B_{2g}/^1B_{2g}$ splitting is considerably larger. Moreover, at the same level of theory, the calculated state ordering for In_2P_2 is quite different from Ga_2P_2, with the $^3B_{2g}$ and $^1B_{2g}$ states lying below the ^3A_u and ^1A_u states [35], even though the anion photoelectron spectra are very similar.

The Ga_3P^- photoelectron spectrum shows well-separated transitions to the ground and first excited states of Ga_3P; the difference in VDEs is 0.96 eV. The excited state peak appears to consist of overlapped transitions to at least two electronic states. This qualitatively agrees with the ab initio calculations which predict Ga_3P to have a $^1A_1$ ground state and a cluster of three excited states, the $^3A_2$, $^3A_1$, and ^1E states starting at $T_e = 2.14$ eV. However, the calculated excitation energies are clearly much larger than in the experimental spectrum. Agreement with theory is better for GaP_3. The peak in the GaP_3^- spectrum at highest electron energy shows transitions to two overlapping states with VDE differences of 0.38 eV; the next peak lies 1.46 eV above the ground state. Feng and Balasubramanian GaP_3 to have a $^3A_2$ ground state with ^1E and ^3E excited states lying 0.36 and 1.07 eV, respectively, above the $^3A_2$ state, with all states having C_{3v} symmetry. The overall agreement supports this calculated ordering of electronic states.

The photoelectron spectra of $Ga_2P_3^-$ and $Ga_3P_2^-$ show that the neutral clusters have essentially the same EA, 3.03 eV. The ground and first excited states of Ga_2P_3 are separated by only 0.21 eV. While only a single large peak is seen in the $Ga_3P_2^-$ spectrum, its irregular shape suggests it represents transitions to at least two overlapped electronic transitions. The experimental spectra are consistent with calculations that predict that the ground and first excited states are nearly degenerate for both neutral clusters. For Ga_2P_3, the trigonal bipyramidal (D_{3h})

${}^2A''_2$ state is calculated to lie only 0.05 eV above the distorted trigonal bipyramidal ${}^2B_1$ state, resulting from Jahn–Teller distortion of a ${}^2E''$ state. In Ga_3P_2, the two lowest-lying states are the distorted trigonal bipyramidal ${}^2A_1$ state and the edge-capped tetrahedral ${}^2B_1$ states, with the ${}^2A_1$ state lying 0.08 eV below the ${}^2B_1$ state; these states result from Jahn–Teller distortion of the D_{3h} trigonal bipyramidal ${}^2E'$ and ${}^2E''$ states, respectively.

5. Larger clusters

Fig. 4 shows a plot of EA vs. the number of atoms for clusters with various stoichiometries. The EAs are plotted as a function of $N^{-1/3}$, where N is the total number of atoms. Clusters with an even number of atoms are shown with solid shapes and odd clusters are represented by open shapes. In general, for a particular stoichiometry Ga_xP_{x+y}, the EA increases with x. Moreover, for clusters with approximately the same number of atoms, odd clusters have higher EAs than even clusters, consistent with our previous work on InP and GaAs clusters [17]. This trend arises because the odd neutral clusters are open-shell species with an odd number of electrons, so that addition of an electron fills an orbital, resulting in a high detachment energy. In contrast, the even neutral clusters are expected to be closed-shell species with lower EAs.

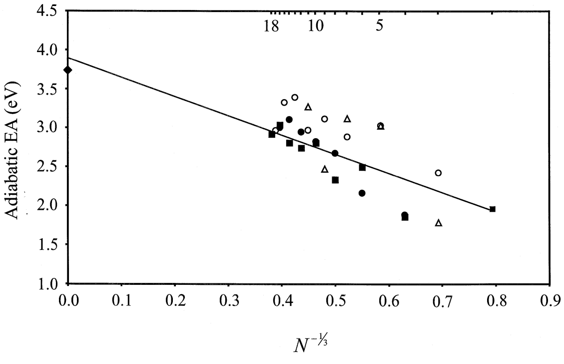

Fig. 4. Plot of the adiabatic electron affinities vs. $N^{-1/3}$, where N is the number of atoms in the cluster. The different stoichiometries are represented by the following symbols: ■ = Ga_xP_x, ● = $Ga_{x+2}P_x$, ○ = $Ga_{x+1}P_x$, △ = Ga_xP_{x+1}, and ◆ = bulk electron affinity.

The overall trend of EA with cluster size is of interest. Photoelectron spectroscopy of metal, semiconductor, and weakly bound clusters have generally shown that above a certain size, the EA smoothly increases and extrapolates to the bulk value. We can estimate the EA of bulk GaP according to the relationship $EA_{bulk} = E_i - E_g$, where E_i ($= 6.01 \pm 0.030$ eV) is the bulk ionization energy and $E_g = 2.272$ eV is the (indirect) band gap at 300 K, yielding $EA_{bulk} = 3.74$ eV. A linear fit to the average EA of the five largest stoichiometric clusters appears to extrapolate to the bulk value. This agrees well with our most recent study of $In_xP_y^-$ clusters in a similar size range [30], although the trend is clearer for indium phosphide clusters. Planned experiments on larger GaP clusters should clarify this trend in the EAs.

Another important trend is the presence or absence of a gap between the transition to the ground state and the first excited state of the neutral cluster. Such a gap is generally present in the even clusters and absent in the odd clusters, particularly for similar stoichiometries. The largest clusters exhibiting this pattern are Ga_7P_7, Ga_8P_7, and Ga_9P_7. The origin of this trend, which was also seen in InP clusters, is related to the even–odd alternation of EAs. Addition of an electron to an even, closed-shell cluster results in a single electron in what was formerly the LUMO of the neutral cluster, and the gap in the resulting anion photoelectron spectrum represents the HOMO–LUMO spacing in the neutral cluster. Odd clusters generally do not show this pattern as the additional electron generally fills a singly occupied orbital in the neutral cluster.

Two further comments regarding the HOMO–LUMO gap are warranted. Previous photoelectron spectra and photodissociation spectra of InP clusters showed that the HOMO–LUMO gap in these clusters was close to the bulk InP band gap of 1.4 eV. However, photoelectron spectra of GaP cluster anions in the same size range are very similar to those of InP clusters, while the band gap of bulk GaP is much larger than that of InP. This indicates that the similarity between the bulk band gap to the HOMO–LUMO gap in small InP clusters is coincidental rather than reflective of some signature of the bulk electronic structure in these very small clusters.

Finally, it appears that clusters with an excess of Ga atoms tend to deviate from the even–odd

HOMO–LUMO pattern. Specifically, the photoelectron spectra of Ga_3P^-, Ga_4P^-, $Ga_4P_2^-$, and $Ga_5P_2^-$ are all similar, with the transition to the electronic ground state of the neutral well separated from transitions to a series of excited electronic states. It appears that the addition of a Ga atom to either Ga_3P or Ga_4P_2 results in little change in the electronic structure of the neutral cluster. It would clearly be of interest to perform ab initio calculations on this series of clusters in order to better understand this observation.

Acknowledgements

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