

III-V semiconductor microclusters: Structures, stability, and melting

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The structural properties of Ga_nAs_n , Ga_nP_n , and Al_nAs_n clusters, $n=2-5$, are determined using the Car-Parrinello method. These *ab initio* results show the existence of a critical size for the advent of alternating arrangements of cations and anions in the case of Ga compounds, in agreement with current interpretations of reactivity measurements. The constant presence of severe undercoordination with respect to the bulk is found in agreement with indications from photoabsorption data on InP. The influence of bond ionicity and size mismatch on the structures of the monatomic isoelectronic clusters is clarified. The effects of temperature are also investigated through simulations of hot (melted) clusters.

The study of the III-V compound semiconductor microclusters is motivated by the great technological interest in the epitaxial growth and interfacial properties of these materials. Experimental results on gas-phase clusters have been recently reported for GaAs (Refs. 1-3) and for InP,⁴ revealing interesting similarities as well as dissimilarities with the bulk materials. In particular, measurements of the reactivity of singly ionized Ga_nAs_n microclusters, $3 \leq n \leq 8$, to ammonia indicate that alternating arrangements of Ga and As must form for $n > 3$ and that their structures must resemble "pieces of crystal surfaces." Moreover, optical absorption of In_nP_n microclusters, $3 \leq n \leq 6$, is characterized by band-bulk-like behavior with a tail at lower energy, strongly sensitive to the size of the clusters and suggestive of the presence of atoms with "severe coordinative unsaturation." In spite of the growing of experimental investigations, theoretical work is lacking. The only exception to our knowledge is a detailed enumeration of possible isomers for aggregates of up to ten atoms (based on the use of combinatorials on some specific high-symmetry polyhedra⁵) and *ab initio* calculations on GaAs and GaAs_2 .⁵

We have applied the *ab initio* molecular-dynamics (MD) Car-Parrinello (CP) method⁶ to study the equilibrium structures of the isoelectronic clusters Ga_nAs_n , Ga_nP_n , and Al_nAs_n , for $2 \leq n \leq 5$, as well as their stability and thermal behavior.⁷ This extensive search enables us (i) to provide a rationale from *ab initio* for the behavior of Ga_nAs_n clusters upon ammonia chemisorption, and for the existence of electronic states below the band gap; (ii) to identify the effect of ionicity on the structures of the monoatomic isoelectron clusters, for which we choose Ge_{2n} as natural reference calculated with the same method;⁸ (iii) to characterize the effect of cationic and anionic substitution, and (iv) to discuss the effect of temperature on the cluster shapes.

As for the computational procedure and previous applications of the CP method to monoatomic clusters, we refer the reader to the literature.^{6,9} Here we use norm-conserving angular-momentum-dependent s , p , and d pseudopotentials,¹⁰ a fcc unit cell of 40 a.u. edge, and an energy cutoff of 11 Ry for the plane-wave expansion.

With this cutoff, we have verified that the structural energy ordering of the bulk solids in the covalent (zinc blende, wurtzite) and ionic (rocksalt) structures is unaltered, and the bond lengths are underestimated by at most 0.1 a.u. with respect to the converged values.¹¹ For the structural optimization we used the dynamical-simulated-annealing (DSA) strategy, analogous to our previous study of silicon microclusters,^{12,13} and supplement it with relaxation of guessed structures via the conjugate-gradients method. Structural optimization for compound clusters turned out to be more complicated than for the monoatomic clusters of the same size, as a result of both the presence of a larger number of possible isomers⁵ and the lower diffusivity of the ions which have more bond constraints to satisfy. Therefore the search for low-energy structures cannot be considered exhaustive. Structural stability was checked with MD runs. As a further check of the accuracy of the calculations we have applied DSA to As_4 and P_4 , which turned out to be tetrahedra in agreement with experiment and with bond lengths equal to the measured values within 2%.¹⁴

We shall now describe the low-energy structures thus determined, and attempt to answer three main questions.

(i) How does the structural pattern at low energy change on passing from Ge_{2n} to Ga_nAs_n ?

(ii) Does the structure have an alternating type of arrangement?

(iii) Can we identify chemical differences among the various isomers?

We recall that, as expected, the low-energy structures of Ge_n clusters (at least up to $n=10$) are the same as those for Si_n ,^{13,15} with a typical increase of 4% in the bond length. However, comparison of the energetics shows that changes in energy orderings may occur and structural energy differences can vary by as much as 50%. The measurable parameters we shall report as possible indications of chemical distinction among different isomers are bond lengths (d_{GaAs} , d_{GaGa} , d_{AsAs}), average distances from the cluster center of the cationic and anionic species (R_{Ga} , R_{As}), average coordination numbers (CN's), as well as energy-band widths. In order to establish the relative

stability of different isomers, both structural energy differences and transition energy barriers are necessary. The former quantities are reported. The calculation of the latter is beyond the scope of this paper. However, in order to investigate possible structural transformations and assess structural stability we have performed specific computer experiments, which we describe below.

Starting from the tetramer, the largest number of isomers possible for the binary clusters in contrast with the monoatomic clusters is evident. However, chemical bonding constraints strongly reduce the choice and actually only one isomer seems to be energetically favored. The ground state is in fact a planar rhombus, as in the case of Ge_4 and Si_4 , with the As—As bond favored and a As—Ga—As bond angle of $\sim 52^\circ$. This result is in agreement with the proposal in Ref. 5. Isomers that favor the Ga—As bond are indeed much higher in energy. We have found two, one three dimensional (3D) and one 2D, which are higher in energy by ~ 0.8 and ~ 1.0 eV, respectively.

Fully analogous to the results on Ge_6 and Si_6 ,¹³ we find for the hexamer that two quasidegenerate structures compete for the ground state [Fig. 1(a)]: an edge-capped trigonal bipyramid (I) and a distorted octahedron (II). The presence of two atomic species of different sizes induces

further distortions such as bending. The most interesting feature is that in both (I) and (II) the Ga-As arrangement is not alternate, in agreement with indications from experiments on the singly ionized clusters.³ In fact, in both cases one As has two As atoms as its nearest neighbors and both Ga-As and As-As strong chemical bonds are present. This is apparent in Fig. 2 where the electron density distribution is displayed [for the case of the (I) structure] on a plane containing one As and two nearest neighbors, of which one is Ga and the other is As. One noticeable difference between (I) and (II) is that in (I) $R_{\text{As}} < R_{\text{Ga}}$ by 0.7 a.u., while in (ii) $R_{\text{As}} \sim R_{\text{Ga}}$. The energy eigenvalues reflect these differences only weakly, the width of the occupied levels decreasing only by 0.2 eV from (I) and (II). We have also considered other isomers: the trigonal prism (TP) and a buckled structure deriving from rapid quench from high temperature and closely connected to the D_{3h} planar compact arrangement of monoatomic clusters. Both of them correspond to a perfectly alternate arrangement of cations and anions and turn out to be high in energy (~ 0.4 eV), in accordance with the case of Ge_6 .⁸ In order to check further the "stability" of the two low-energy isomers we have performed several simple "experiments." In particular, if we exchange all the Ga and As atoms in the (I) structure and

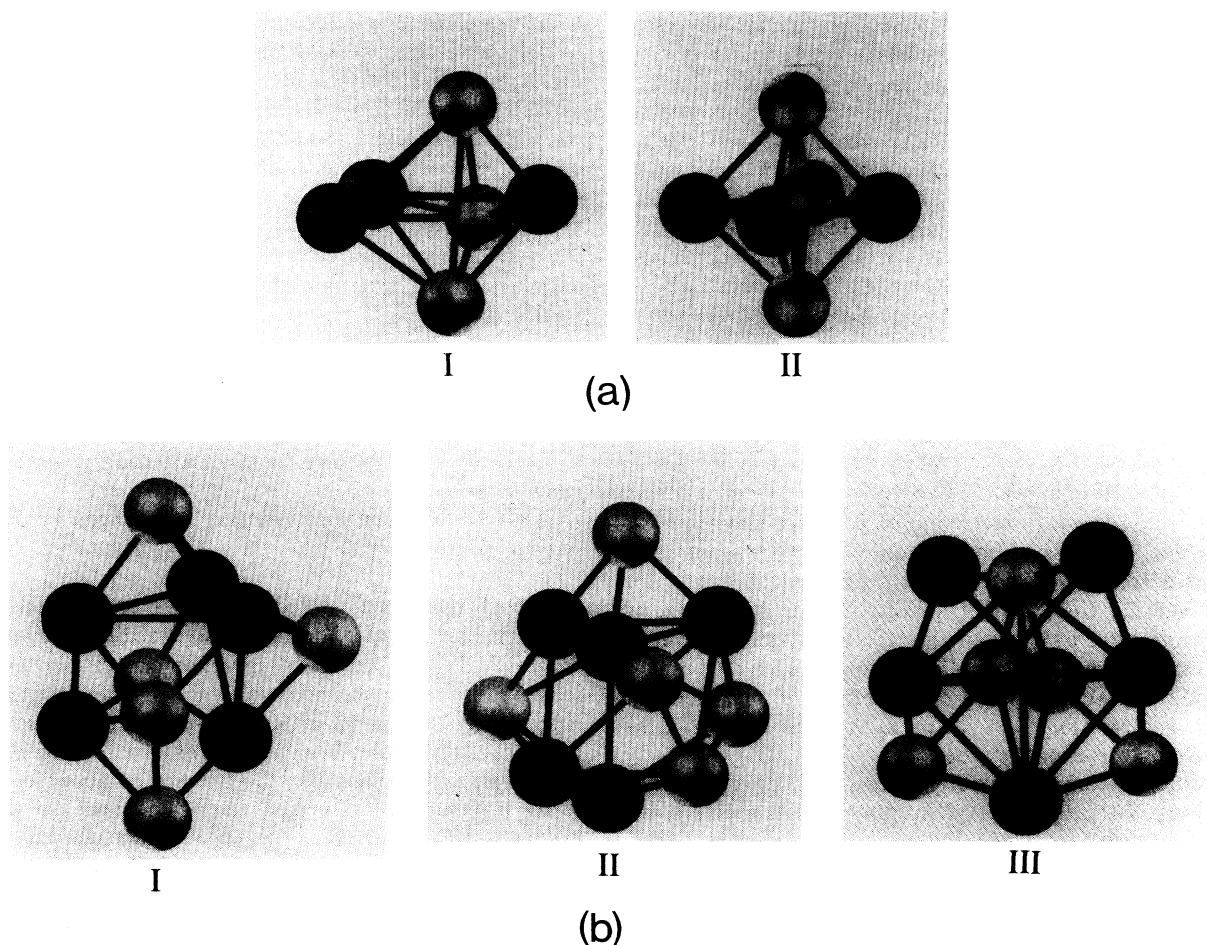


FIG. 1. Structures of (a) Ga_3As_3 and (b) Ga_5As_5 (see text).

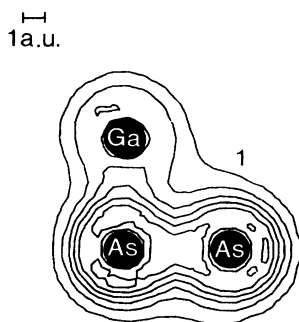


FIG. 2. Ga_3As_3 (I): planar projection of the electron-density distribution (see text). Units: $0.01 e/(\text{a.u.})^3$.

let them relax, we find that such a configuration (higher by ~ 0.7 eV) spontaneously transforms to (I). If we, instead, construct an alternate type of arrangement over the frame of the (I) structure (which corresponds to exchanging one Ga with one As) we find that this spontaneously transforms to (II).

In the case of the octamer, we have only relaxed structures generated by capping in different ways an octahedron, educated by the knowledge of the lowest-energy structures of Ge_8 (Ref. 8) and Si_8 .^{13,15} Structures derived from capping with trans-caps remain lower in energy (by at least 0.5 eV) than those derived from capping with skewed caps (which generally implies stronger distortions). The preferred arrangement is not of the alternate type, and is characterized by a coordination number of 3 for the As atoms, with two Ga—As and one As—As bonds.

The decamer is the most remarkable of the clusters considered. Figure 1(b) illustrates three structures: (I) is the result of the annealing, (II) and (III) correspond to the relaxation and optimal distribution of Ga and As on the frame of the two low-energy structures of Si_{10} ,¹³ i.e., the tetracapped trigonal prism and the tetracapped octahedron, respectively. (I) can be described as a distorted bicapped dodecahedron. In the case of Ge_{10} (II) is the lowest-energy structure as for Si_{10} , followed by (I) at 0.85 eV and then by (III) at 1.1 eV. In Si_{10} , instead, (III) is at 0.65 eV and (I) at 0.84 eV. Ga_5As_5 has a different energetics, (I) and (II) being quasidegenerate and (III) higher by 1.2 eV. These differences reflect a very interesting chemistry. In particular, it is clear why (I) and (II) are favored in the case of GaAs: Such geometries allow the anions to have an optimal average CN of 3 with a Ga—As CN of 2.6, while in (III) the latter is strongly reduced. Also, we note that in both (I) and (II) $R_{\text{As}} \geq R_{\text{Ga}}$ [by 1.2 a.u. in (I) and 0.5 a.u. in (II)], while in (III) $R_{\text{Ga}} > R_{\text{As}}$ by ~ 0.8 a.u. We have verified that (III) is unstable upon exchange of Ga and As; in fact, after relaxation, (III) is spontaneously recovered. We have also considered ionic-type structures, such as the one suggested for Na_5Cl_5 in Ref. 16. This distorts and ends up in a high-energy minimum which keeps all the characteristics of the ionic type of structure and implies in particular a CN of 3 for Ga—As and no As—As chemical bond. An important result is that in the lower-energy isomers of Ga_5As_5 an alternate Ga and As arrangement is favored,

in contrast to what happens in the hexamers. This is again in agreement with the interpretation of reactivity measurements upon ammonia chemisorption.³

On passing from GaAs to GaP, we find, as expected, an overall similarity, i.e., the same energy ordering for the structures discussed above and a bond-length decrease of about 4%, in full analogy with the results for the bulk.¹⁷ The only remarkable differences are seen¹⁸ (i) in the hexamer where the energy gap separating the TP and the quasiplanar isomers from the ground-state structure increases to ~ 0.8 eV, and (ii) in the octamer, where different arrangements of cations and anions on the Ge_8 frames (both alternate and not) turn out to be quasidegenerate.

By substituting Ga with Al in the As compounds, more profound changes occur, although, in a given structure, both the bond length and the radii of the two species remain almost the same.¹⁸ In particular, we find that (i) the energy ordering of the four structures considered for Ga_3As_3 changes, the D_{3h} (here planar) and the TP being almost degenerate and lower than the (I) and (II) structures [Fig. 1(a)] by ~ 0.3 eV; (ii) in Al_4As_4 , the energy gap between structures derived from trans-capped and skewed-capped octahedra decreases significantly; and (iii) in Al_5As_5 , the (II) structure [Fig. 1(b)] becomes higher in energy [0.65 eV above (I)] and almost degenerate with the isomer derived from the Na_5Cl_5 structure. The presence of planar structures at lower energy as well as the constant preference for alternate arrangements are in agreement with the fact that the Al—As bond is more ionic than the Ga—As bond. In the calculations for the bulk solids this is reflected in the fact that, under pressure, the rocksalt structure is more stable for AlAs.¹⁷ For the sake of comparison, we recall that ionic compound clusters such as Na_3Cl_3 are planar rings.¹⁶

We have studied the effects of temperature for the ten-atom cluster of GaAs by performing several simulations of hot clusters, starting from different configurations.¹⁸ Although the time of observation was very limited (up to 5 psec) for drawing final conclusions, we can summarize the main observations as follows: (i) The As ions show a tendency to be on the outside of the cluster as illustrated in Fig. 3. (ii) Other characteristics of the low- T isomers are also retained, i.e., the Ga—As CN oscillates about 2.4 with a narrow fluctuation of 0.2, only a few As—As chemical bonds are present and the arrangement is still alternate. (iii) The mobility of the cation appears to be higher, in agreement with the results of simulations of l -GaAs.¹⁹ However, the estimated diffusion coefficient for Ga in Ga_5As_5 at 1500 K is one order of magnitude smaller than in the bulk.

Calculations on Ga_8As_8 reveal characteristics similar to Ga_5As_5 .¹⁸ Trying to understand (i), we point out that an electronic mechanism favors configurations where the “surface” atoms are those to which charge is transferred. As another manifestation of the same phenomenon, we recall that the GaAs (110) surface presents buckling with the As atoms on the outermost layer.

In the case of Ga_5P_5 we also observe preference for structures with the anions on the outside of the clusters at least at low temperatures. However, within our short

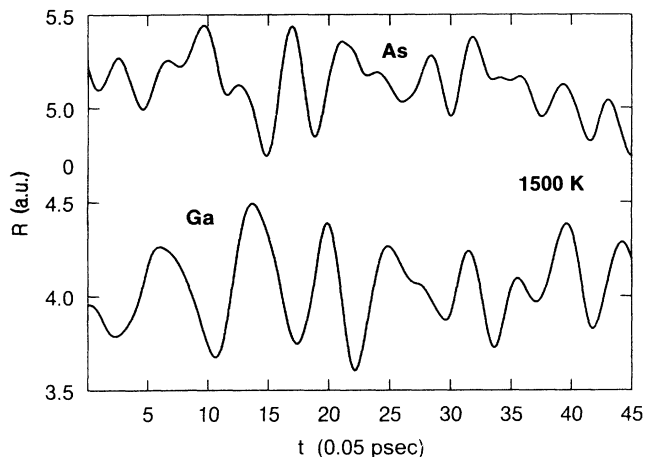


FIG. 3. Ga_5As_5 at high T : time variation of R_{Ga} and R_{As} .

simulation times, we find, for instance, that the system can be trapped in strongly segregated configurations with Ga atoms on the surface. We note that in this case the mismatch between the cation and the anion covalent radii is not negligible. Therefore size effects, which tend to put the larger species (here Ga) on the surface of the cluster,²⁰ oppose the electronic mechanism. This may be the reason why the energy barriers between configurations with P on the inside of the clusters and those with P on the outside are much higher than in the case of GaAs.

In conclusion, we have presented a comparative structural study of the III-V compound stoichiometric 1:1 microclusters in the size range up to ten atoms. Although the search for the low-energy minima of their complex potential-energy surface cannot be considered exhaustive, the comparison with Si and Ge as well as among three compounds enables us to draw a few conclusions. One clear result is that, in order to determine the relevant structures of the binary semiconductor clusters, simple alternate "decoration" of the monoatomic isoelectronic clusters, although being a good first approximation, is not sufficient. This comes mainly from the presence of strong anion-anion bonds which involve non-

trivial distortions and may not favor the alternate type of configuration. We find that this requires a critical size for the Ga compounds, in agreement with suggestions from experiment.³ For the neutral clusters, this is 5 for As and 4 for P. Our results indicate that a change in the size dependence of reactivity to NH_3 must be expected in the case of AIAs. Also, in agreement with indications from photoabsorption data on InP,⁴ we find that in this size range "severe undercoordination" exists and indeed all the atoms are undercoordinated with respect to the bulk. This is in contrast to the case of the monoatomic aggregates, which in the size range 6–10 appear to prefer slightly overcoordinated configurations.¹³

It also emerges from these calculations that in the small aggregates the difference of chemical bonding in the three compounds is emphasized with respect to the bulk. This must be attributed to the greater availability of structures compared with the bulk solid, and only in part to specific size effects on the bonding. Beyond the specific realm of cluster physics, we believe that this comparative study of microaggregates may be relevant for the study of localized defects in III-V ternary compounds and may provide hints as to the understanding of interfacial chemical disorder in $\text{GaAs-Ga}_{1-x}\text{Al}_x\text{As}$ heterostructures.²¹

The next step of this investigation will be the study of nonstoichiometric III-V semiconductor clusters, which will make our picture of the chemical bonding in these materials more complete. This will also enable us to calculate dissociation energies and to estimate probable fragmentation channels. This information, however, will not be sufficient to get insight into the important issue of the formation and fragmentation processes, for which kinetic effects must be calculated. This is, however, still beyond the feasibility of *ab initio* simulations.

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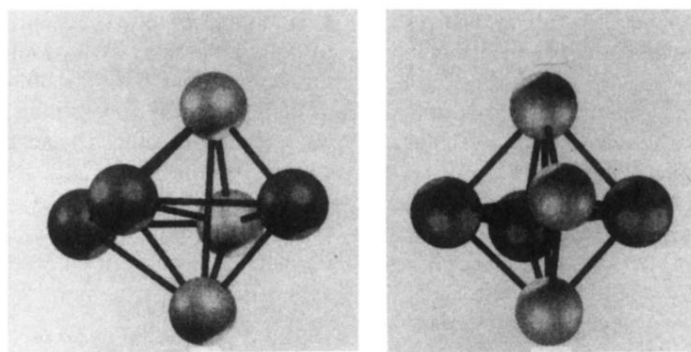
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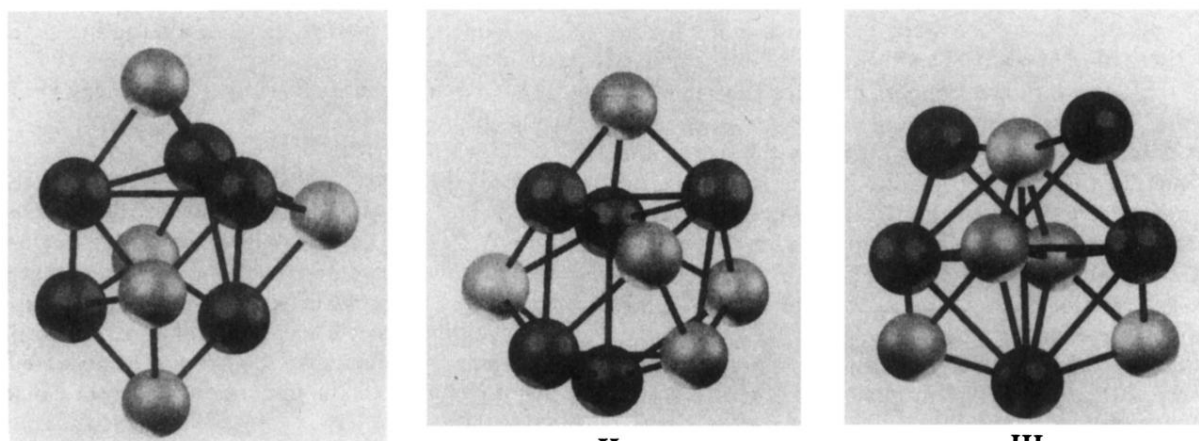
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I (a) II



I II III (b)

FIG. 1. Structures of (a) Ga_3As_3 and (b) Ga_5As_5 (see text).