

Polymerization of molecular (yellow) arsenic

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Abstract

DTA studies were performed to investigate the polymerization of molecular (yellow) arsenic (y-As), in the dark and also under illumination/irradiation. The semiempirical quantum chemical CNDO/BW method for calculating the dimerization reaction pathway of two As_4 molecules was applied, and showed that the stability of y-As decreases, due to the formation of stable fragments of the polymeric phase (a-As). Using the principle of orbital symmetry conservation, it was shown that polymerization takes place most favourably from a staggered “face-to-face” configuration of As_4 molecules. Dark polymerization proceeds under activation. For a result of the initial stage of polymerization, CNDO/BW simulation predicts the formation of an As_8 dimer. The molecular cluster As_8 of D_{2h} symmetry forms a six-membered chair-shaped ring which constitutes one of the dominating units in the polymeric phase (a-As).

Keywords: Yellow arsenic; Polymerization; CNDO/BW; As_4 ; As_8 cluster

1. Introduction

Elements of Group V, in particular P, As, and Sb, possess an ns^2np^3 electron configuration in the outer shell and are thus capable of forming three σ -bonds positioned in an orthogonal arrangement, which determines the possibility of forming tetrahedral molecules, X_4 . Another possible arrangement consists of the formation of a pyramidal configuration XX_3 , the three-coordinated bonds being capable of closing into a continual random network [1]. A further structural possibility, observed in metallic arsenic, is formation of a layer-like structure which has been investigated in great detail previously [1–4]. These peculiarities

determine the possibility of a large choice of interatomic and intermolecular packings, thus leading to a large variety of possible allotropic states, which is a specific property of the elements of Group V of the Periodic System.

Molecular or yellow arsenic (y-As) was first reported by Bettendorff in 1864 [5] who obtained it from solution in CS_2 into which As vapour was introduced. It deposited itself at the bottom of the vessel if cooled down to $-70^\circ C$. The layer thus obtained was identified as a yellow modification of arsenic in the form of molecular crystals, the molecular mass corresponding to As_4 molecules. The specific density was determined as approx. 2 g cm^{-3} [6], which is about three times smaller than that of metallic arsenic. It was found to be an analogue of white phosphorus, considerably more unstable than the latter.

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γ -As may be obtained by deposition of four-atomic tetrahedral As_4 molecules from the gaseous phase on cooled substrates. Depending on the condensation temperature, γ -As may exist in several crystalline and non-crystalline states [7]. The high-temperature phase of γ -As forms a plastic crystal with orientationally disarranged molecules, owing to the rotation of the latter [8]. This form of the plastic state is characteristic of molecular crystals (including white phosphorus P_4 [9]) which are formed from highly symmetrical molecules.

All molecular modifications of arsenic are metastable, being limited at the high temperature side by irreversible transitions, each within its own temperature range. The phenomenon of such phase transitions is unusual, since they take place between two metastable states of arsenic, the final stage of these being the amorphous disordered structure.

Yellow arsenic reveals photosensitivity over a wide spectral range. Under the effect both of illumination (visible region) and irradiation (UV, X-rays, particles) and on heating, irreversible changes take place in the molecular structure of yellow arsenic (γ -As), i.e. bond switching between the As_4 molecules, with formation of a covalently bonded molecular network of amorphous arsenic or the so-called polymeric state of arsenic. These photostructural changes constitute the basis of image formation on γ -As layers [10].

During recent decades, amorphous arsenic (α -As), which is a typical model example for the amorphous state of matter, has been widely studied [1]. The structural unit of α -As is formed by a trigonal pyramid AsAs_3 . The rules of spatial arrangement of such pyramids are well described by the statistics of even-odd rings in the continuous random network (CRN) model [11]. Such a CRN model describes satisfactorily the structure of bulk α -As (β -As) which is usually obtained omitting the stage of molecular arsenic.

The polymerization of γ -As under the effect of illumination/irradiation, or on heating, presents a multistage process. The starting stage of molecular cluster formation is of particular interest, i.e. the study of the reaction pathway of the interaction among tetrahedral As_4 molecules.

It is natural to assume that the potential energy hypersurfaces in the reaction between a molecular pair will be different depending on the kind of molecular packing in different γ -As modifications. Even in the disordered phase of γ -As, which exists up to 80 K, the As_4 molecules are oriented pairwise in staggered “face-to-face” configuration, whilst there is certain disorder in the mutual orientation between molecular pairs [12]. As a result of the reaction, we observe cleavage and switching of bonds between the As_4 molecules, with formation of intermediate molecular clusters. Into this process, molecules from the nearest surroundings get involved, which leads to the creation of the neighbouring phase, which is thermodynamically more stable in the bulk of γ -As. This mechanism of thermo- and photopolymerization was first proposed by us in Ref. [13].

In the course of recent decades, special experimental and theoretical studies have been carried out concerning small molecules and clusters in the gaseous phase of elements of the VA group of the Periodic System. This interest was enhanced by the synthesis of qualitative epitaxial semiconducting films of III–V materials. In the quenched vapour of phosphorus at 300 K, Martin [14] identified molecular clusters of P_n up to $n = 24$. Small and medium clusters of P, As and Sb have been investigated quantum-chemically, and their equilibrium geometry has been determined [15–24]. Häser et al. [20], using as an SCF energy base for clusters up to $n = 28$, proposed a probable reaction scheme for the formation of red phosphorus from white phosphorus units and proposed possible structural units for red phosphorus. Hohl and Jones [24], using density functional and molecular dynamics methods, simulated the polymerization of 26 P_4 molecules in the liquid state to a disordered network.

In the present work, DTA methods and CNDO/BW quantum chemical calculations of the potential hypersurface of the reaction pathway have been applied for further studies of thermo- and photostimulated polymerization of the molecular modification of γ -As [25,26]. The interaction between As_4 molecules has been approached on the basis of the Woodward–Hoffmann principles [27].

2. Details of the method

2.1. DTA sample preparation

The calorimetric studies of vacuum-deposited γ -As layers were performed in a Calvet-type microcalorimeter, specially adapted for investigating heat phenomena in thin deposited layers at low temperatures [7]. The samples of the γ -As high-temperature modification [7] were prepared using the procedure as in Refs. [25,26], which is briefly described below.

Yellow arsenic layers were deposited in a separate vacuum cryostat. The substrate temperature could be kept steady from liquid nitrogen temperature up to approx. 400 K. The layers under study were deposited on the cleaned inner surface of a thin-walled copper cylinder of 20 mm diameter and 50 mm height. They were then transferred into the measuring chamber of the DTA device. A similar copper cylinder, of the same mass as the first one, was placed into the reference chamber. The cryostat is provided with channels for irradiating the samples with X-rays and light at condensation temperature. The deposition was carried out in vacuum, (10^{-5} Torr), in the dark. The condensation temperature was maintained at 200 ± 2 K, the temperature of the source was 330°C , the rate of growth of the layer was approx. 18 \AA s^{-1} , the sample mass was approx. 120 mg, the sample thickness was approx. $20 \mu\text{m}$. The starting material consisted of metallic rhombohedral arsenic with a total impurity content less than 10 ppm. Since metallic arsenic oxidizes readily in air, particularly in the presence of water vapour, the material was heated in vacuum at 200°C prior to evaporation, in order to remove traces of arsenic oxide. The purified material was then resublimed. After preparation of the sample, the cryostat was de-evacuated with dry nitrogen, and the copper cylinder containing the substrate with the deposited layer was transferred into the microcalorimeter chamber which had previously been brought to the condensation temperature. The samples were monitored by means of the DTA curve. The amount of heat release in the exo- and endothermic processes must be in proportional dependence to the mass of the sample; the

ratio $\Delta H_{\text{endo}}/m$ and $\Delta H_{\text{exo}}/m$ must be kept constant.

Irradiation of the γ -As layers obtained was carried out inside the cryostat, under a nitrogen atmosphere. For irradiation with X-rays, an X-ray tube with a Cu anode was used, for the $K\alpha$ radiation of which the layer thickness for half-attenuation exceeds $30 \mu\text{m}$. Such a radiation interacts with the layer material uniformly throughout the whole bulk.

Illumination of the γ -As samples by strongly absorbed light with approx. 2.5 eV photon energy was effected in the process of their preparation in vacuum. A xenon tube was used as a source, the IR and red part of its emission spectrum being filtered off by means of a constant-flow 10% CuSO_4 solution. The total illumination dose was $1.2\text{--}30 \text{ J cm}^{-2}$ in various measurement series. This exceeded by several orders of magnitude the dose value necessary for producing a photographic effect in γ -As [10].

2.2. CNDO/BW calculation

Quantum chemical modelling of equilibrium molecular clusters of arsenic (interacting molecules As_4 and the molecular As_8 dimer) was performed with the aid of the modified version of the semiempirical CNDO/BW method [28]. The program requires calibration of the two-centre parameters α_{xy} and β_{xy} over given values of structural characteristics and the binding energy of the 2- and 4-atomic molecules As_2 and As_4 . For optimization of the molecular structure geometry, the Fletcher–Powell procedure was used. The method of cyclic coordinate descent provides independent variation up to 10 internal or Cartesian coordinates. In addition, synchronous scanning of a number of independent internal coordinates permits modelling of various types of intramolecular vibrations.

Potential hypersurface fragment calculation and binding energy estimates in the equilibrium state were carried out for the case of two As_4 molecules and of the chair-shaped As_8 cluster. For each of the molecular configurations, it was also possible to obtain the valence electron density distribution $\rho(\mathbf{r})$, as well as the energy spectra of one-electron

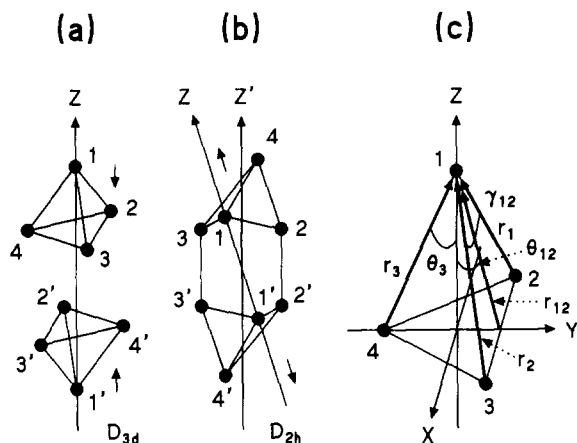


Fig. 1. Initial configuration of systems consisting of two As_4 molecules (a) and of the cluster As_8 (b); (c) shows the molecular coordinates used in the CNDO/BW calculation. The Z' axis is chosen for convenient visualization of the As_8 configuration of D_{2h} symmetry.

states $N(\epsilon)$. CNDO/BW calculations were performed for the singlet ground states of both molecular particles in the sp-base of the valence electrons.

The Z -axis was chosen as the basic axis of the dimerization reaction, this axis passing through the uppermost atoms of the interacting As_4 molecules (Fig. 1a) and through those of the reaction product As_8 (Fig. 1b). CNDO/BW simulation of the molecular particle structure was carried out in two opposite scanning directions along the Z -axis: in the direction of approach (Fig. 1a) of two interacting As_4 molecules (the initial symmetry of the reaction path being D_{3d}), and in the direction of extension (Fig. 1b) of the chair-shaped configuration of the molecular cluster As_8 (the final symmetry of the reaction path being D_{2h}). During the course of motion along the coordinates, independent variation of the five pairs of internal coordinates was ensured, namely of $r_1 (= r_2)$, γ_{12} , θ_{12} , r_3 and θ_3 (Fig. 1c), where $r_1 = r_2$ is the $\text{As}(1) - \text{As}(2)$ or the $\text{As}(1) - \text{As}(3)$ distance, r_3 is the $\text{As}(1) - \text{As}(4)$ distance, $\langle \gamma_{12} = \langle (r_1 r_2) \rangle$ is the valence angle between $\text{As}(2) - \text{As}(1) - \text{As}(3)$ atoms, $\langle \theta_{12} = \langle (r_{12} Z) \rangle$, and $\langle \theta_3 = \langle (r_3 Z) \rangle$ are the Euler angles of the As_4 molecules or of the pyramid-shaped As_8 cluster. Continuous variation of these coordinates in the course of optimizing the

geometry of the approaching two As_4 molecules and of the cluster As_8 provided for constancy of the symmetry of the dimerization reaction pathway as a minimum within the framework of the D_{2d} point symmetry group. In addition, at certain Z values, an azimuthal rotation was performed on one of the pyramid-shaped fragments AsAs_3 with respect to the other one.

3. Results

3.1. DTA studies

Fig. 2 shows DTA curves obtained from a freshly prepared γ -As layer (a), and from a layer after irradiation by X-rays (b), and one illuminated in the course of preparation (c). The DTA curve for

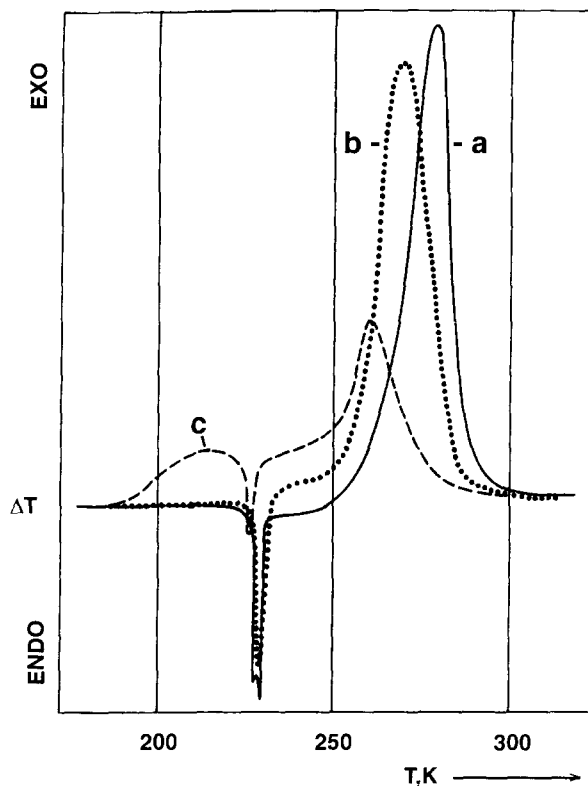


Fig. 2. DTA curves of yellow arsenic prepared at 200 K: a, before illumination (solid line); b, after irradiation by X-rays (dotted line); c, illuminated in the course of preparation (dashed line).

a freshly prepared sample reveals two well-defined singularities: an endothermic heat effect at $T = 227$ K, due to a reversible transition into the plastic phase, characterized by disordered orientation of As_4 molecules through rotation around the C_3 axis, and an irreversible exothermic effect with extrapolated onset at 250 K, with maximum heat release at 280 K, due to polymerization of molecular arsenic [8,25]. The plastic phase of γ -As exists within a very narrow temperature range of approx. 20 K, as confirmed by IR spectroscopy methods [7].

The applied X-ray dose produced structural changes in about 5% of the material, which distributed themselves uniformly throughout the bulk of the latter. As may be seen from Fig. 2(b), irradiation leads to a shift of the exothermic peak by approx. 10 K towards lower temperatures, and to distortion of the low-temperature branch of the DTA curve. This suggests that the exothermic transition, namely the polymerization of γ -As, proceeds against the background of a weak additional heat release. The onset of this additional heat release determined by the point of deviation of the DTA curve from the baseline, lies near 210 K. The position of the endothermic peak remains practically unchanged, whilst the process itself proceeds against the background of additional heat release.

The additional heat release is still more marked in the case of large exposures in DTA measurements, when part of the polymerized amorphous phase becomes, under the effect of illumination, comparable with the amount of the initial γ -As. Such samples were obtained by intensive illumination in the process of deposition and growth of the γ -As film (Fig. 2(c)). The curve shows a clearly defined low-temperature exotherm, as well as the usual exo- and endothermic peaks for γ -As. From the peak intensities, the γ -As content can be estimated at 30%. The peak of the polymerization exotherm shifts, as expected, towards lower temperatures with respect to the position shown in Fig. 2(b). Marked additional heat release sets in at approx. 180 K, reaching maximum value at approx. 220 K.

At temperatures between around 250 K and room temperature, as may be seen from Fig. 2(a) and (c), we observe an irreversible exothermic effect

which is a result of dark polymerization in non-illuminated molecular arsenic. We consider polymerization to be due to the relatively low stability of the tetrahedral molecules of As_4 with 60° bonding angles, due to “banana”-type strained bonds. Such bent strained bonds are also characteristic of tetrahedral molecules of the Group V elements, starting with phosphorus. This is a result of the ns^2np^3 electron configuration possessing characteristic $np\sigma$ bond angles, which exceed 90° in all compounds of these elements [29].

The excess energy of strain of the molecular tetrahedron is removed in the process of bond cleavage and switching between the As_4 molecules. This results in a change in the type of structure elements: the tetrahedral molecules As_4 disappear, and instead we observe an appearance of trigonal pyramid-shaped structure units AsAs_3 , with different bonding angles and lengths. We get one of the possible states of a covalently bonded network of α -As. The enthalpy of the transformation ΔH , as obtained in our DTA measurements [25], is 7.1 ± 0.5 kJ mol $^{-1}$. The main contribution to this value, as we have shown in Ref. [26], is due to the strain energy of the tetrahedral molecules.

The relative stability of γ -As at low temperatures is determined by the existence of an energy barrier. The activation energy E_a necessary for surmounting the barrier may be found from the relation connecting the temperature of the maximum of the exothermic DTA peak, i.e. the temperature of the maximum rate of transition, T_m , with the heating rate. We used heating rates in the DTA measurements, the values of which lay between 1.2 and 0.25 K min $^{-1}$. The range of chosen rates is limited at the top by the requirement of maintaining quasi-stationary temperature conditions in the calorimeter. The choice of the lower boundary of the heating rate in the DTA method is limited by the considerably diffuse nature of the exothermic peak, which makes quantitative treatment of the data rather difficult. For the description of the kinetics of polymerization, the phenomenological equation of Avraami $\ln(\nu/T_m) = -E_a/kT_m - \ln A_0$ was used for the case of crystallization of amorphous arsenic [1]. The dependence of $\ln(\nu/T_m)$ on $1/T_m$, where ν is the heating rate, T_m is the maximum of the exopeak temperature, is linear, as may be seen

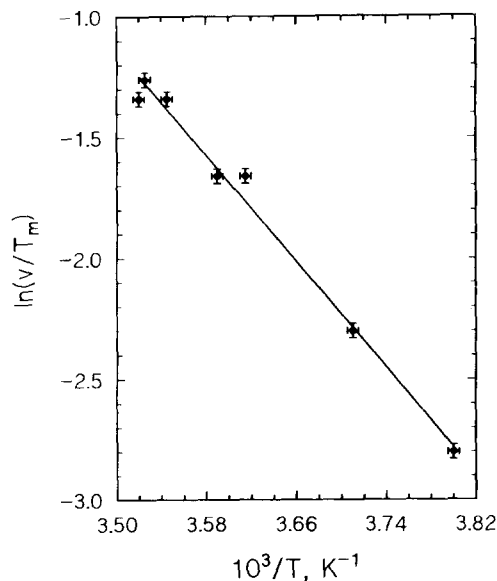


Fig. 3. Dark polymerization of yellow arsenic is an activation process. Determination of activation energy from the $\ln(\nu/T_m)$ dependence on $1/T_m$.

from Fig. 3. The slope of this dependence with respect to the abscissa yields the value of the activation energy E_a , equalling 0.48 ± 0.07 eV.

3.2. Analysis of the reaction pathway

The details of the initial stage of polymerization have not been quite clear up to now. In this paper, we propose a basic path of the polymerization reaction in γ -As. The process starts by interaction between two As_4 molecules. A characteristic

structural property of the α -As network is the existence of poly-membered rings. In particular, the weight proportion of six-membered rings, predicted by the Greaves and Davis model [11], is high and equals 22%. With the aid of Fig. 4(a), one may follow up the appearance of a six-membered ring in “face-to-face” interaction between two As_4 molecules in staggered configuration. An analysis in terms of orbital symmetry conservation can be easily performed according to the Woodward–Hoffmann principles [27]. Fig. 4(b) presents a correlation diagram of a polymerization reaction between two As_4 molecules, as well as the reaction product, a six-membered ring. The bonds break between 2 and 3 and 4 and 5, and form between atoms 2 and 5 and 3 and 4. As a result of the reaction, we obtain a six-membered ring interclosing the atoms 1–2–3–4–5–6. The classification of the combinations of the orbitals of breaking and newly forming bonds according to symmetry has been performed in the following manner. For symmetry elements, two planes were taken, with respect to which the MO of two As_4 and of the reaction products were classified. The breaking bonds are crossed by one plane, the newly formed plane and the other plane (Fig. 4(a)). The symmetric S and antisymmetric MO A are classified with respect to these planes. Juxtaposition of the molecular MO and the MO of the six-membered ring shows that the highest occupied SA orbital of the molecules does not correlate with the highest occupied AS orbital of the product. At the same time, we observe crossing of the occupied

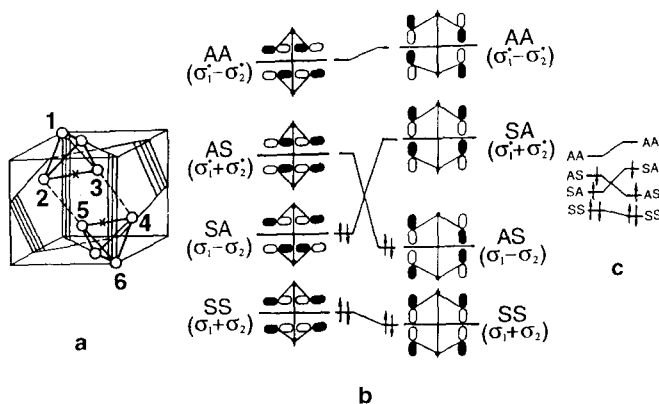


Fig. 4. Correlation diagram: a, for the polymerization reaction of As_4 molecules; b, in the ground state; c, in the excited state.

orbitals of the reacting molecules with the anti-bonding orbital of the product. This means that the given reaction may be regarded as forbidden by symmetry in the ground state and may take place only through activation. If, however, the polymerization reaction proceeds under conditions of photoexcitation and is effected through empty lowest excited states, then we have complete correspondence by symmetry of all states occupied by electrons (Fig. 4(c)). This means that the reaction is permitted by symmetry in the excited state and will take place without activation.

Correlation diagrams, constructed accounting for other possible configurations of As_4 molecular pairs, show that polymerization reactions are forbidden by symmetry for any state of reagent and product. This means that the reaction proceeds either by activation or with participation of radicals [27]. As shown by Daniel and Leadbetter [12], polymerization of γ -As prepared at approx. 30 K produces a structure which is similar to that of α -As. Hence, molecular packing in the staggered “face-to-face” configuration is the most favourable one for the start of a polymerization process and is characterized by a low activation barrier (polymerization at around 80 K).

3.3. CNDO/BW calculation of the dimerization pathway

A detailed study has been performed of the reaction pathway of two As_4 molecules in staggered “face-to-face” configuration (see Fig. 4a). The CNDO/BW dimerization pathway of As_4 is demonstrated in Fig. 5. The ordinate E_{bind} corresponds to binding energy values of optimized configurations of two approaching As_4 molecules (curve (a) in Fig. 5), and at the extension of the molecular As_8 cluster (curve (b) in Fig. 5). Modelling of the geometry with the aid of an optimization procedure indicates the existence of an equilibrium structure of the dimer As_8 in D_{2h} symmetry, which possesses the lowest binding energy. The dimerization reaction $2\text{As}_4 \rightarrow \text{As}_8$ is endothermic. The molecular cluster As_8 is 183 kJ mol^{-1} less stable with respect to 2As_4 . Ballone and Jones [23] and Jones and Hohl [21] performed density functional calculations combined with molecular dynamics of

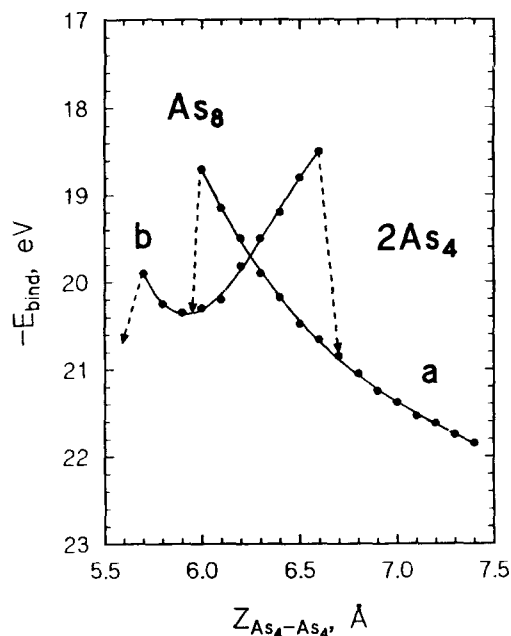


Fig. 5. Projection of fragments of potential binding energy hypersurface upon the $E_{\text{bind}}-Z$ plane for the reaction pathway $2\text{As}_4 \rightarrow \text{As}_8$ (a) and $\text{As}_8 \rightarrow 2\text{As}_4$ (b).

As_n and P_n clusters with $n = 3-11$ and also showed that As_8 (D_{2h}) and P_8 (D_{2h}) are less stable with respect to 2As_4 and 2P_4 by 15 kJ mol^{-1} and 31 kJ mol^{-1} respectively. A similar conclusion was made for the form P_8 (D_{2h}) by Häser et al. [20] who studied P_n ($n = 4-28$) clusters by ab initio SCF/MP2 calculations.

Both binding energy curves (a) and (b) of the molecular particle dimerization reaction, as shown in Fig. 5, intersect at a point corresponding to the value $Z_c = 6.23 \text{ Å}$. Moving along the curve (a) in the direction towards $Z < Z_c$ leads to Hartree–Fock instability (HFI) [30], and, finally, to a leapwise transition $E_a(Z) \rightarrow E_b(Z)$, as indicated by the arrow on curve (a). A similar effect may be observed on moving along curve (b) at $Z > Z_c$. An analysis of the distributions $\rho(r)$ and $N(\epsilon)$ confirms the assertion about the presence of HF instability. The phenomenon of the “impossibility of selfconsistent solutions” occurs in semi-empirical calculation methods of molecules without sufficient inclusion of configurational interactions [30]. Halevi et al. [17], in their studies of the $2\text{P}_4 \rightarrow \text{P}_8$ (O_h) dimerization reaction by the

MNDO method, also pointed out the appearance of HFI. The authors of Ref. [17] came to the conclusion that the interval in the vicinity of Z_c corresponds to the intermediate configuration of a P_8 cluster in the reaction $2P_4 \rightarrow P_8$.

We also wish to point out that in the course of deformation of the cluster As_8 (D_{2h}) (which consists of a $D_{2h} \rightarrow D_{2d}$ transition), we observe a curve possessing a different minimum binding energy (left arrow on curve (b)). The configuration obtained corresponds to an almost cubic structure of the cluster As_8 , possessing O_h symmetry. CNDO/BW calculations show that the As_8 (O_h) cluster is more stable, as compared to two As_4 molecules by 14 kJ mol^{-1} , which agrees with ab initio calculation results [18] and with MNDO [17] results for phosphorus P_8 (O_h). The existence of cubic pnictide clusters is, in our opinion, doubtful. Our CNDO/BW calculations yielded an unjustified high binding energy value for As_8 (O_h). This is, most likely, due to disregard of the repulsion effect of parallel bonds in a cube-shaped cluster. Such a possibility has been pointed out previously in Refs. [16] and [21]. A more detailed discussion of the polymerization reaction path of As_4 will be considered in a later paper.

4. Discussion

From the point of view of informativity, the polymerization of γ -As ought to be studied under illumination or irradiation. The photoinduced shift towards lower temperatures of the exothermic peak and the rise of its low-temperature branch of the DTA curve (Fig. 2(b)) indicates lowering of the stability of γ -As caused by illumination. Such an effect is necessarily produced by active centres, i.e. inclusions of the neighbouring phase. According to Raman studies, the short-range order structure of illuminated γ -As is very close to that of α -As [31]. Accordingly, the polymerization of γ -As proceeds in a mixed system of the molecular and photopolymerized phases. The breaking up of the system into coexisting phases is connected with a widening of the dividing boundaries between the latter, and, accordingly, with a growing of the sites with atypical As atom coordination, including unsaturated

dangling bonds, i.e. paramagnetic centres [32]. In the unstable γ -As matrix these active centres, possessing increased reactivity, form nucleation centres and enhance polymerization in their direct neighbourhood. Judging the size and structure of the polymeric phase fragments is rather difficult. ESR studies [32] only show that the shape and position of ESR signals in the spectrum of illuminated arsenic, which can be singled out in the complex spectrum in the course of illumination, are very close to those observed in α -As [33]. This only shows that the local structures of the nearest surroundings of the paramagnetic centres upon newly formed fragments in illuminated γ -As and in α -As are sufficiently close.

With increase in illumination exposure, we observe in the system an increasing domination of that part of the material which has undergone photostructural changes (Fig. 2(c)). Illumination leads to both an enlargement of the photopolymerized phase fragments, and to an increase in their number. The moving boundaries of the fragments contain an excess, with respect to the equilibrium concentration, of broken and dangling bonds, and will capture molecules in their surroundings. This permits an interpretation of the low-temperature exotherm at 200–250 K as a thermal response to the switching of dangling bonds and final bonding between the fragments of the photopolymerized phase.

The photopolymerization reaction may be considered, within the framework of the correlation diagram (Fig. 4(c)), as one of the channels of removal of excitation. This may correspond to the transfer of an electron onto an antibonding orbital of the neighbouring molecule and to the formation of an intermediate state of a bonded electron-hole pair [10]. Such excitation destabilizes the As_4 molecules, which, in addition, possess excess energy of strained bonds.

Polymerization of γ -As in the process of heating the layers without illumination proceeds through activation. Applying the principle of minimum displacement of groups of atoms and that of orbital symmetry conservation after Woodward and Hoffmann, we have performed an analysis of possible reaction pathways of two As_4 molecules, and have shown that the most advantageous approach is for

molecules positioned in staggered “face-to-face” configuration. If the molecules are excited and if the electron transfer takes place on an antibonding orbital of the neighbouring molecule, then polymerization proceeds without activation. Cleavage and switching of one bond takes place in each molecule. As a result, an intermediate molecular cluster As_8 is formed, of chair-like shape and of symmetry D_{2h} ; such a possibility agrees with our quantum chemical calculations of the dimerization reaction path between two As_4 molecules (Fig. 5). The existence of isolated molecular clusters As_8 and P_8 has also been confirmed by energy calculations using the density functional method [21–23] and by ab initio SCF/MP2 calculations [20]. The packing of As_4 molecules in a staggered “face-to-face” configuration has been registered for the case of γ -As obtained by condensation of As vapour at 30 K [12]. Polymerization takes place at very low temperatures (approx. 80 K), which may take place with insignificant displacement of atoms and at low activation energy.

Approach from other molecular configurations, “apex-to-face” or “edge-to-edge”, is forbidden by orbital symmetry for any state of the molecules. These configurations are, apparently, energetically less advantageous, since they require inclusion of additional rotational degrees of freedom on the way towards staggered “face-to-face” configuration, i.e. towards the onset of the reaction path of D_{3d} symmetry. In this case, polymerization requires a higher activation energy and proceeds at higher temperatures. For our crystalline [7,25] molecular arsenic obtained at 200 K condensation temperature, the beginning of transition sets in at 250 K, and the experimentally determined activation energy value equals 0.48 eV.

Our CNDO/BW calculations show that a chair-shaped isolated As_8 cluster (D_{2h}) is less stable than $2As_4$. Polymerization of arsenic in a condensed molecular state is an exothermic process. Release of heat energy equal to the energy bond strain in the molecule, as a result of photo- or thermotransition may stimulate drawing of neighbouring As_4 molecules into the polymerization process. The further cascade of As_4 molecule addition to the As_8 leads to the formation of a large cluster, in which the number of strained three-membered

rings will decrease. Such a cluster may be present as a stable fragment of the polymeric phase of arsenic. Similar and, to our opinion, promising polymerization schemes for white phosphorus have been discussed in Ref. [20], on the basis of SCF energy considerations of molecular clusters. One of the schemes forecasts possible polymerization reaction paths through interaction between P_4 molecules only. Stable red phosphorus aggregates may be formed through addition of P_4 molecules to the wedge-shaped P_8 cluster (C_{2v}), as well as joining two P_8 molecules themselves by two single bonds.

The formation of intermediate molecular clusters As_n with an odd number of atoms is also possible. Initially they contain twofold coordinated atoms (dangling bonds). Such a possibility is indicated by the experimentally observed molecular clusters P_n , with n up to 24 [14], similar to arsenic. These were obtained by annealing red phosphorus vapour in a helium stream. Quantum chemical calculations by the density functional method also confirm the existence of stable clusters of phosphorus P_9 and P_{11} , containing a twofold coordinated bridge atom [22]. The authors of Ref. [22] report that a similar tendency also takes place with respect to large arsenic clusters.

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