

## Photostimulated structural changes in yellow arsenic

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 5805

(<http://iopscience.iop.org/0953-8984/7/29/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:45

Please note that [terms and conditions apply](#).

## Photostimulated structural changes in yellow arsenic

A Rodionov, R Kalendarev and J Eiduss

Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063 Riga, Latvia

Received 8 February 1995, in final form 24 March 1995

**Abstract.** DTA and ESR methods were applied for studying photostimulated changes in molecular arsenic ( $\gamma$ -As). It is shown that under the effect of illumination/irradiation the stability of  $\gamma$ -As decreases, which is due to the formation of stable fragments of the polymeric phase ( $\alpha$ -As). Using the principles of orbital symmetry conservation, it is shown that polymerization takes place most favourably from a staggered 'face to face' configuration of  $\text{As}_4$  molecules. Photopolymerization may proceed without activation. As a result we get a formation of an intermediate molecular cluster  $\text{As}_8$  of 'chairlike' symmetry  $D_{2h}$ .

### 1. Introduction

Yellow arsenic reveals photosensitivity over a wide spectral range. Under the effect of illumination (visible region) and irradiation (UV, x-rays, particles), irreversible changes take place in the molecular structure of yellow arsenic ( $\gamma$ -As)—bond switching between the  $\text{As}_4$  molecules, with formation of a molecular covalently bonded network of amorphous arsenic or the so-called polymeric state of arsenic. These photostructural changes constitute the basis of image formation on  $\gamma$ -As layers [1].

During the last few decades amorphous arsenic ( $\alpha$ -As), which is a typical model example for the amorphous state of matter, has been widely studied [2]. The structural unit of  $\alpha$ -As is formed by a trigonal pyramid  $\text{AsAs}_3$ . The rules of spatial arrangement of such pyramids are well described by the statistics of even-odd rings in the model of a continual random network (CRN) [3]. Such a CRN model describes satisfactorily the structure of bulk  $\alpha$ -As ( $\beta$ -As) which is usually obtained omitting the stage of molecular arsenic.

Yellow or molecular As ( $\gamma$ -As) may be obtained by deposition of four-atom tetrahedral  $\text{As}_4$  molecules from the gaseous phase on cooled substrates. Depending on the condensation temperature,  $\gamma$ -As may exist in several crystalline and non-crystalline states [4]. The high-temperature phase of  $\gamma$ -As forms a plastic crystal with orientationally disarranged molecules, owing to rotation of the latter [5]. This form of the plastic state is characteristic of molecular crystals (including white phosphorus  $\text{P}_4$  [6]) which are formed of 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.

It might be of considerable interest to investigate the initial stage of the polymerization of  $\gamma$ -As under the effect of heat or illumination/irradiation, in other words, the reaction paths of  $\text{As}_4$  molecule interaction. It is natural to assume that the potential energy surfaces in the reaction between a molecular pair will be different depending on the kind of molecular

packing in different  $\gamma$ -As modifications. Even in the unordered phase of  $\gamma$ -As, which exists up to 80 K, the  $\text{As}_4$  molecules are oriented pairwise in staggered 'face to face' configuration, whilst there is certain disorder in the mutual orientation between molecular pairs [7]. As a result of the reaction we observe cleavage and switching of bonds between the  $\text{As}_4$  molecules, with formation of intermediate molecular clusters. In 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  $\gamma$ -As. This mechanism of thermo- and photopolymerization was first proposed by us in [8].

The present work presents results of further studies of photostimulated changes in the molecular modification of  $\gamma$ -As by DTA and ESR methods. The approach employed is based on the Woodward-Hoffmann principle [9].

## 2. Experimental details and sample preparation

The calorimetric studies of vacuum-deposited  $\gamma$ -As layers were performed in a Calvet-type microcalorimeter, specially adapted for investigating heat phenomena in thin deposited layers at low temperatures. Our DTA device had a maximum sensitivity of  $6 \mu\text{W}$  with respect to heat emission within the 90–420 K range. All measurements were carried out at a heating rate of  $1 \text{ K min}^{-1}$  [4].

Yellow arsenic layers were deposited in a separate vacuum cryostat. The substrate temperature could be kept steady from liquid nitrogen temperature up to  $\sim 400 \text{ K}$ . The layers under study were deposited upon the cleaned inner surface of a thin-walled copper cylinder of 20 mm diameter and 50 mm height. The latter was 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 vacuo*,  $\sim 10^{-5}$  Torr, in the dark. The condensation temperature was maintained at  $200 \pm 2 \text{ K}$ , the temperature of the source was  $330 \text{ }^\circ\text{C}$ , the rate of growth of the layer was  $\sim 18 \text{ \AA}^{-1}$ , the sample mass was  $\sim 120 \text{ mg}$ , the sample thickness was  $\sim 20 \mu\text{m}$ . The starting material consisted of metallic rhombohedral arsenic with 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 vacuo* at  $200 \text{ }^\circ\text{C}$  prior to evaporation in order to remove traces of arsenic oxide. The purified material was then resublimated. The weighed amounts of the material were kept in evacuated glass ampoules ready for use. 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  $\gamma$ -As layers obtained showed good adhesion to the substrate surface and did not contain inclusions of nonmolecular arsenic which had served as the vapour source. The samples were monitored by means of the DTA curve. The amount of heat release in exo- and endoprocesses must be in proportional dependence on the mass of the sample; the ratio  $\Delta H_{\text{endo}}/\text{mol}$  or  $\Delta H_{\text{exo}}/\text{mol}$  must be kept constant. Crack formation of  $\gamma$ -As films could be observed sometimes at temperatures exceeding 280 K, in the form of 'noise' on the declining part of the exothermic DTA curve. The films started showing cracks in the transition process, after more than half of the sample had polymerized.

Irradiation of the obtained  $\gamma$ -As layers was carried out inside the cryostat, in nitrogen atmosphere. For irradiation with x-rays, an x-ray tube with a Cu anode was used, for the  $\text{K}\alpha$  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  $\gamma$ -As samples by strongly absorbed light with  $\sim 2.5$  eV photon energy was effected in the process of their preparation *in vacuo*. As a source a xenon tube was used, the IR and red part of its emission spectrum being filtered off by means of a constant-flow 10%  $\text{CuSO}_4$  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  $\gamma$ -As [1].

For ESR measurements the  $\gamma$ -As samples were prepared by means of deposition on a 'Spex' Mylar film  $3\ \mu\text{m}$  thickness, which does not yield a paramagnetic signal of its own. The Mylar film was kept in position by electrostatic forces on the inner surface of a copper cylinder. After preparation of the samples in the cryostat by the method described above, the cylindrical container with the sample was transferred into liquid nitrogen, where the film with the  $\gamma$ -As layer was rolled into a tube by means of a special device and placed into a standard quartz ESR cuvette. All operations were conducted under a liquid nitrogen layer. The ESR cuvettes with the samples were also kept in liquid nitrogen before the beginning of the measurements.

The ESR spectra of the  $\gamma$ -As samples under investigation were registered by means of a RE13-06 radiospectrometer. The determination of the paramagnetic centre content was performed according to [8] at liquid nitrogen temperature, as well as in the temperature range between 100 and 370 K, maintained by blowing through nitrogen vapour.

### 3. Results and discussion

#### 3.1. DTA and ESR studies

Figure 1 shows DTA curves obtained from a freshly prepared  $\gamma$ -As layer (a), and from a layer after irradiation by x-rays (b). The DTA curve for 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  $\text{As}_4$  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 [5]. The plastic phase of  $\gamma$ -As exists within a very narrow temperature range of  $\sim 20$  K, as confirmed by IR spectroscopy methods [4].

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 figure 1(b), irradiation leads to a shift of the exothermic peak by  $\sim 10$  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  $\gamma$ -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 base line, lies near  $\sim 210$  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 the amount of the polymerized amorphous phase becomes, under effect of illumination, comparable with the amount of the initial  $\gamma$ -As. Such samples were obtained by intensive illumination in the process of deposition and growth of the  $\gamma$ -As film. The DTA curve obtained by illumination, applying strongly absorbed light, during preparation of the layer is presented in figure 2. The curve shows a clearly defined low-temperature exotherm, as well as the exo- and endothermic peaks usual for  $\gamma$ -As. From the peak intensities one may estimate the  $\gamma$ -As content at 30%. The peak of the polymerization exotherm shifts,

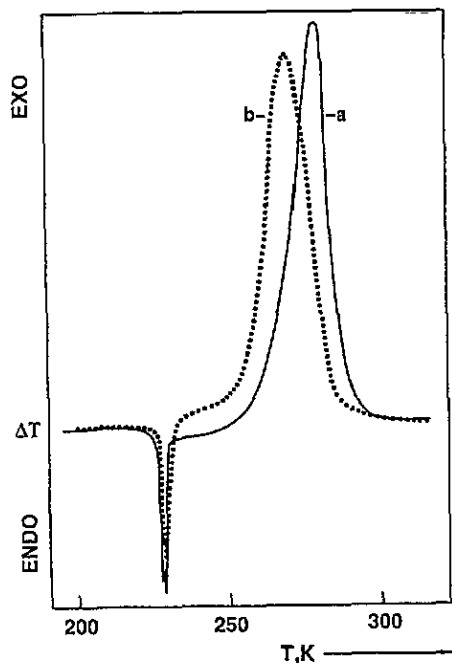


Figure 1. DTA curve of yellow arsenic: (a) before irradiation (—); (b) after irradiation with x-rays (••••).

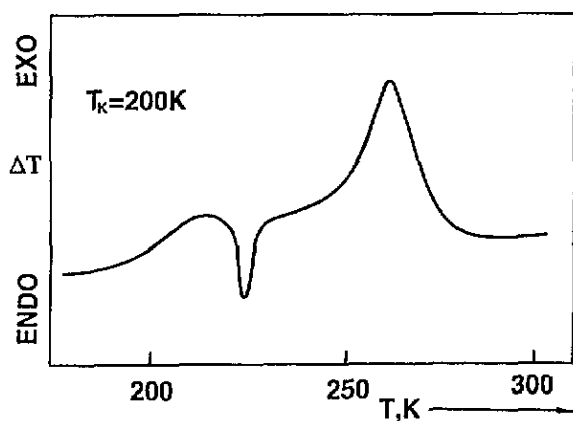


Figure 2. DTA curve of yellow arsenic illuminated in the course of preparation.

as expected, towards lower temperatures with respect to the position shown in figure 1. Marked additional heat release sets in at  $\sim 180$  K, reaching a maximum value at  $\sim 220$  K.

In order to elucidate the nature of photoinduced changes in  $\gamma$ -As, ESR measurements were undertaken on illuminated samples. Illumination conditions corresponded to those described above for the case of DTA measurements. Accordingly, the molecular modification content also could be estimated at 30%. The ESR signal of illuminated samples is close in shape and position in the spectrum to the ESR signal of a completely polymerized arsenic layer obtained by dark polymerization [10]. The paramagnetic centre content was estimated at  $\sim 8 \times 10^{18}$  spins  $\text{cm}^{-3}$ , as shown in figure 3. Heating the samples from 140 K to 370 K at a rate of  $\sim 1$  K  $\text{min}^{-1}$ , we observe a monotonic decrease of the photoinduced ESR line, with a subsequent dramatic drop to  $1 \times 10^{18}$  spins  $\text{cm}^{-3}$  at  $\sim 220$  K. Further rise in temperature leads to a diminution in the paramagnetic centre content, however, with different kinetics. This corresponds to the temperature interval between 250 K and 370 K.

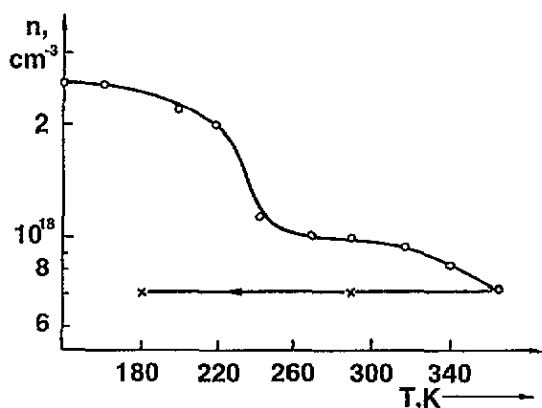


Figure 3. Temperature dependence of paramagnetic centre content in yellow arsenic, illuminated in the course of preparation.

In this temperature range the polymerization process of the remaining molecular part of the sample is completed. Annealing at 370 K leads to constant paramagnetic centre content in a completely polymerized sample, namely  $\sim 7 \times 10^{17}$  spins  $\text{cm}^{-3}$ , in fair agreement with [11].

It might be worth recalling, what stable paramagnetic states of arsenic mean. As we showed in [10], the ESR signal of the initial  $\gamma$ -As is due to dark paramagnetic centres, localized on molecular clusters and on fragments of the amorphous (polymeric) phase. In both cases the paramagnetic centres are formed by two-coordinated As atoms, the dangling bonds of which contain a lone electron ( ${}_pP_2^0$ ). For the case of  $\alpha$ -As these centres have been studied in detail [11]. It was found in our quantum chemical CNDO/BW calculations [12] that molecular clusters  $As_n$  are relatively stable in the  $\gamma$ -As matrix for  $n > 5$ , containing a dangling bond, and possess a diminished number of strained bonds and three-membered rings, as compared to the  $As_4$  molecule. The wave function of a lone electron is basically of p nature, with a small s-contribution ( $\sim 1$ –2%). The contribution of the lone electron to the wave function yields the p orbital of the two-coordinated As atom, as well as of the two first and the two neighbouring atoms. As a result of thermal polymerization, to which we have the corresponding exothermic peak in figure 1(a), we also observe a change in the paramagnetic states in  $\gamma$ -As. These changes are well manifested in the transformation of the dark ESR signal [10].

A photoinduced shift of the exothermic peak towards low temperatures and the rise of its low-temperature shoulder on the DTA curve (figure 1(b)) indicates lowering of stability of the  $\gamma$ -As, due to irradiation. That is just the effect to which active centres—inclusions of the neighbouring phase—must lead. According to Raman studies of illuminated  $\gamma$ -As, its near-order structure and that of  $\alpha$ -As are very similar [13]. Therefore polymerization of  $\gamma$ -As takes place in a mixed system of molecular and photopolymerized phase. The disintegration of the system into coexisting phases is due to widening of the boundaries between the phases, hence to an increased number of sites for As atoms with non-typical coordination, including dangling unsaturated bonds, viz. paramagnetic centres  ${}_pP_2^0$ . In the unstable  $\gamma$ -As matrix these active centres, possessing increased reactivity, are bound to act as centres of nucleation and enhance polymerization processes in its nearest surroundings. To draw conclusions about the sizes and structure of polymer phase fragments is rather difficult. One can only state that the shape and position in the ESR signal of the illuminated  $\gamma$ -As samples, which can be singled out of the total complex spectrum during the illumination process, is very close to that observed in  $\alpha$ -As [10]. It only shows that the local structures of the nearest surroundings of paramagnetic centres in the fragments newly formed in

illuminated  $\gamma$ -As and in  $\alpha$ -As are sufficiently close.

With increasing illumination exposure the proportion of the material which has undergone structural changes begins to dominate in the system (figure 2). Illumination causes increase in both size and number of the photopolymerized phase fragments. The moving boundaries of the fragments will contain an excess of dangling bonds, as compared to their equilibrium content, and will capture surrounding molecules. At the contact between the fragments the separating boundaries may remain intact, since not all dangling bonds will be under conditions energetically favourable for bond switching. As may be seen in figure 3, the temperature region of the first drop in the paramagnetic centre content ( $\sim 200$ – $250$  K) coincides with the temperature region of the additional isothermic process in figure 2. Such a correlation makes it possible to interpret the low-temperature isotherm as a thermal response to the switching of dangling bonds and final bonding between the fragments of the photopolymerized phase.

At temperatures between  $\sim 250$  K and room temperature, as may be seen from figures 1(a) and 2, we observe an irreversible exothermic effect which is a result of dark polymerization in non-illuminated molecular arsenic. The observed ESR centres are more stable, and their content equals  $\sim 1 \times 10^{18}$  spins  $\text{cm}^{-3}$ . Such a concentration characterizes, as previously shown in [8], the polymerized state of arsenic. We consider polymerization to be due to the relatively low stability of the tetrahedral molecules of  $\text{As}_4$  with  $60^\circ$  bonding angles, due to 'banana'-type strained bonds. Such bent strained bonds are also characteristic of tetrahedral molecules of the elements of group V, starting with phosphorus. This is a result of the  $ns^2np^3$  electron configuration possessing characteristic  $np\sigma$  bond angles, which exceed  $90^\circ$  in all compounds of these elements [14].

The excess energy of strain of the molecular tetrahedron is removed in the process of bond cleavage and switching between the  $\text{As}_4$  molecules. This results in a change in the type of structure elements: the tetrahedral molecules  $\text{As}_4$  disappear, and instead we observe an appearance of trigonal pyramid-shaped molecules  $\text{AsAs}_3$ , with different bonding angles and lengths. We get one of the possible states of a covalently bonded network of  $\alpha$ -As. The enthalpy of the transformation, as obtained in our DTA measurements [15], equals  $\Delta H = 7.1 \pm 0.5$  kJ  $\text{mol}^{-1}$ . The main contribution to this value, as will be shown in the appendix, is due to the strain energy of the tetrahedral molecules.

### 3.2. Analysis of the reaction path

The details of the initial stage of polymerization have not been quite clear up to now. We are now going to propose the basic path of the polymerization reaction in  $\gamma$ -As, as it appears to us. The process starts by interaction between two  $\gamma$ -As molecules. A characteristic structural property of the  $\alpha$ -As network is the existence of polymembered rings. In particular, the weight proportion of six-membered rings, predicted by the Greaves and Davis model [3], is high and equals 22%. With the aid of figure 4(a) one may follow up the appearance of a six-membered ring in 'face to face' interaction between two  $\text{As}_4$  molecules in staggered configuration. An analysis in terms of orbital symmetry conservation can be easily performed according to the Woodward–Hoffmann principles [9]. Figure 4(b) presents a correlation diagram of a polymerization reaction between two  $\text{As}_4$  molecules, as well as the reaction product—a six-membered ring. The bonds break between 2–3 and 4–5 and form between atoms 2–5 and 3–4. 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  $\text{As}_4$  and of the reaction product were classified. The breaking bonds are crossed by one plane, those newly formed by the other one (figure 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 orbitals of the reacting molecules with the antibonding 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 (figure 4(c)). This means that the reaction is permitted by symmetry in the excited state and will take place without activation.

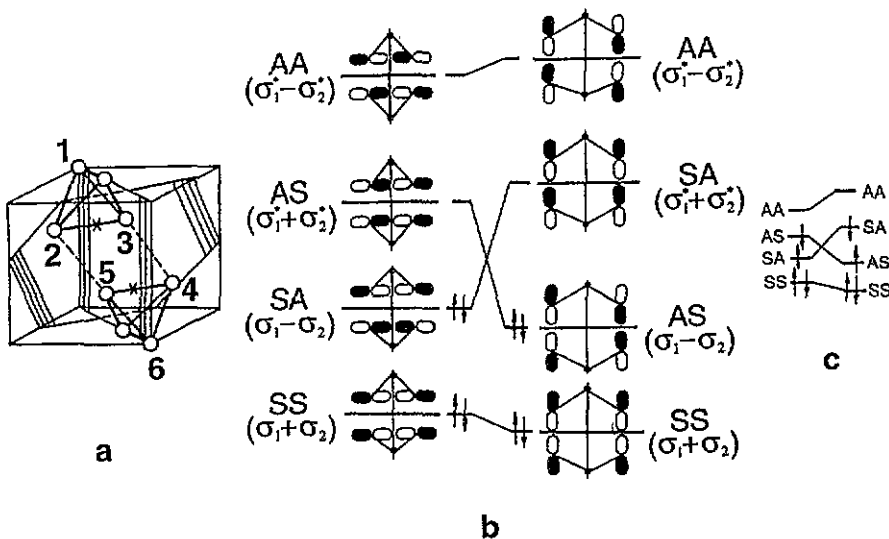


Figure 4. Correlation diagram: (a) for the polymerization reaction of  $\text{As}_4$  molecules; (b) in the ground state; (c) in the excited state.

Correlation diagrams constructed, accounting for other possible configurations of  $\text{As}_4$  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 [9]. As shown by Daniel and Leadbetter [7], polymerization of  $\gamma$ -As at  $\sim 30$  K produces a structure which is similar to that of  $\alpha$ -As. Hence, molecular packing in 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  $\sim 80$  K). A reaction between molecules with different configurations, is, apparently, energetically less viable, since it requires inclusion of additional rotational degrees of freedom on the path towards staggered 'face to face' configuration. In this case, a considerable polymerization rate ought to be observed at higher temperatures, as has actually been found by us with  $\gamma$ -As obtained at 200 K (polymerization with extrapolated onset at  $\sim 250$  K). Additional rotation and displacement of molecules during the reaction path may cause incomplete bond switching, i.e. leads to the appearance of dangling and unsaturated bonds responsible for paramagnetism in arsenic layers.



Photopolymerization reactions in  $\gamma$ -As may form, within the framework of the correlation diagram under consideration (figure 4(c)), one of the possible channels for removing excitation. In molecular arsenic this might correspond to electron transfer onto the antibonding orbital of the neighbouring molecule and to the appearance of an intermediary state of a bonded electron-hole pair [1]. Such an excitation destabilizes the  $\text{As}_4$  molecules possessing also excess strained bond energy. As a result of bond switching an intermediate molecular cluster of  $\text{As}_8$  is formed possessing 'chair-form',  $D_{2h}$  symmetry. The possibility of the existence of such isolated clusters of phosphorus  $\text{P}_8$  has been suggested by quantum chemical calculations of cluster energy by SCF [16] and density functional [17] methods. Calculations show that a 'chair-shaped' isolated  $\text{P}_8$  ( $D_{2h}$ ) cluster is less stable with respect to  $2\text{P}_4$ . Polymerization in the condensed molecular state of arsenic is an exothermic process. Release of heat energy, which is equal to the energy of molecular bond distortion due to photo- or thermopolymerization, may stimulate involvement of neighbouring  $\text{As}_4$  molecules into the polymerization process. A further cascade of  $\text{As}_4$  molecule addition to  $\text{As}_8$  leads to the formation of a large-size cluster, with decreasing relative content of strained three-membered rings. Such a cluster may form a stable fragment of the polymeric phase of arsenic. Similar and, in our opinion, promising schemes of polymerization of white phosphorus have been discussed in [16], based on SCF energy estimates in molecular clusters. One of the schemes predicts possible paths of polymerization of phosphorus through interaction of  $\text{P}_4$  molecules only. Stable aggregates of red phosphorus may form, by addition to the 'wedge-shaped'  $\text{P}_8$  ( $C_{2v}$ ) cluster of  $\text{P}_4$  molecules, as well as by the joining of the  $\text{P}_8$  themselves by two single bonds.

#### 4. Conclusion

In the present work photostimulated transformations in condensed molecular arsenic have been studied by DTA and ESR methods. Under the action of light marked weakening of stability can be observed in  $\gamma$ -As. The exothermic polymerization process shifts by  $\sim 10$ – $20$  K towards lower temperatures, and its integral intensity falls. At the same time, we observe a rise in the intensity of the additional peak of heat release at  $\sim 220$  K, with increase in the illumination dose. The change in stability of  $\gamma$ -As under the action of illumination is, in our opinion, due to the appearance of stable fragments of the neighbouring polymeric phase. Applying the principle of minimum displacement of groups of atoms, as well as that of the Woodward-Hoffmann principle of orbital symmetry conservation, we have analysed possible paths of reactions between two  $\text{As}_4$  molecules, i.e. the initial stage of polymerization. It was shown that the most favourable situation consists in the interaction between molecules in staggered 'face to face' configuration. If the molecules are in an excited state, and we have a charge transfer upon an antibonding orbital of the neighbour, polymerization proceeds without activation. We get cleavage and switching of one bond in each molecule. As a result, an intermediate molecular cluster  $\text{As}_8$  is formed, possessing 'chair-shaped' configuration of symmetry  $D_{2h}$ . Packing of  $\text{As}_4$  molecules in 'face to face' staggered configuration has been observed in  $\gamma$ -As obtained by condensation of vapour at  $\sim 30$  K [7]. Its polymerization takes place at a very low temperature of  $\sim 80$  K, which corresponds to very insignificant atomic shifts and at low activation energy.

Interaction between other molecular configurations—such as 'vertex to face', 'edge to edge'—are forbidden by orbital symmetry in any molecular state and require serious atomic regroupings. Polymerization will demand higher activation energy and will proceed at higher temperatures, as may be observed in the case of our crystalline [4, 15] molecular arsenic obtained at  $\sim 200$  K condensation temperature and having the starting point of transition

at  $\sim 250$  K. The growing clusters of the polymeric phase contain, as shown by our ESR measurements, owing to steric hindrance, an increased content of dangling and nonsaturated bonds in the two-coordinated arsenic atoms. Bonds are restored between the combining fragments of the polymeric phase in the illuminated subsystem of the molecular material already at a temperature below 250 K.

Photostimulated formation of molecular intermediate clusters  $As_n$  is also possible, possessing an odd number of atoms which initially possess two-coordinated atoms (dangling bonds). Such a possibility is suggested by experiments with phosphorus [18] which is an analogue of arsenic. Clusters of phosphorus  $P_n$  with  $n$  up to 24 have been obtained by quenching vapour of red phosphorus in a helium flow. In addition, quantum chemical calculations, applying the density functional method, show the existence of stable phosphorus clusters  $P_9$  and  $P_{11}$  with a two-coordinated bridge atom [19]. The authors of [19] report that a similar tendency takes place also in the case of large arsenic clusters.

Finally, we wish to note that photostimulated transformations may become a promising method for obtaining various amorphous states of arsenic (as well as of P and Sb).  $\gamma$ -As possesses, depending on the chosen modification, one or other kind of molecular packing. Accordingly, the various CRNs forming in the process of the photopolymerization must possess their peculiarities. The first to notice the specificity in the structure of  $\alpha$ -As obtained through polymerization of As deposited at 30 K were the authors of [7]. The advantage of this approach consists in the circumstance that photopolymerization takes place at low temperatures under conditions of relative stability of the molecular modification with a definite packing scheme of molecules. In addition, there exists the possibility that under photopolymerization we may observe a stabilization of the newly formed amorphous phase clusters of medium and large size in the bulk of molecular arsenic. These clusters possess an increased amount of sites with an anomalous coordination of atoms.

### Acknowledgments

The authors express their gratitude to Dr A Shendrick for valuable aid in conducting ESR measurements, and to Dr A Sazonov for permitting us to quote unpublished data on the crystalline structure of  $\gamma$ -As.

### Appendix. The enthalpy of polymerization

Let us attempt an estimate of enthalpy change  $\Delta H_a$  in the polymerization of yellow arsenic. We shall apply the method of valence field forces which has produced satisfactory agreement with experimental data in the estimation of the enthalpy of  $\alpha$ -As crystallization [2]. We assume that the polymerization enthalpy is basically determined by the energy of the strained bonds in the  $As_4$  molecule. Electron diffraction data on As vapour show that the  $As_4$  molecule possesses a tetrahedral angle of  $60^\circ$ , the distance between the atoms equalling  $2.42 \text{ \AA}$  [20]. It is, however, more feasible in the case of an  $As_4$  molecule, owing to the 'banana' shape of the bonds, to consider the maximum of electronic density as lying outside the straight line connecting two arsenic atoms in the molecule (cf. figure A1). This concept of bent bonds was proposed in [21] for  $P_4$ . It is natural to assume that the real angles between the bonding electron pairs and the length of the bonding banana-shaped bond must be considerably larger than the tetrahedral ones. According to the theory of repulsion between electron pairs [14], each arsenic atom with  $4s^2 4p^3$  configuration is capable of producing valence bonds with at least  $90^\circ$  angles, characteristic of orbitals up to tetrahedral

angles as large as 109°. An anomalously small angle equalling 91.8° has been observed in the case of AsH<sub>3</sub>.

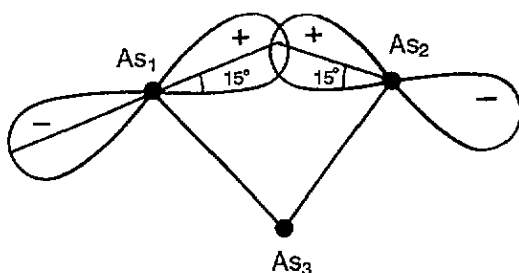


Figure A1. Schematic representation of As-As bent or 'banana' bond, as described in text.

In order to assess the distortion energy, let us assume that the real angle between 'banana-shaped' bonds is the smallest possible in arsenic chemistry, viz.  $\sim 90^\circ$ . The corresponding bond length equals 2.52 Å (figure 5). In the polymeric phase of arsenic the mean angle in the AsAs<sub>3</sub> pyramid equals 98°, the bond length being  $\sim 2.48$  Å [2]. As a result of structural changes the mean bond angle increases by  $\sim \Delta\theta = 8^\circ$ , and the bond length diminishes by  $\Delta r = 0.04$  Å. The strain energy of the As<sub>4</sub> molecule may be written down as follows:

$$E = \frac{1}{2}k_\theta r^2(\Delta\theta)^2 + \frac{1}{2}k_r(\Delta r)^2$$

where  $k_\theta$  is the bond bending force constant, equalling 11 N m<sup>-1</sup> [2], and  $k_r$  is the bond stretching force constant equalling 120 N m<sup>-1</sup> [22]. Since the coordination number of the arsenic atoms equals three, and each bond is divided between two atoms, i.e.  $\Delta H_u = \frac{3}{2}E$ , we obtain the polymerization enthalpy of  $\gamma$ -As equal to  $\Delta H_u = 6.8$  kJ mol<sup>-1</sup>. This value is in fair agreement with the experimental enthalpy value, namely  $7.1 \pm 0.5$  kJ mol<sup>-1</sup> [15].

## References

- [1] Sazonov A I, Kalendarev R I and Eiduss J A 1983 *Zh. Nauch. Prikl. Fot. Kin.* **28** 334
- [2] Greaves G N, Elliot S R and Davis E A 1979 *Adv. Phys.* **28** 49
- [3] Greaves G N and Davis E A 1974 *Phil. Mag.* **29** 1201
- [4] Kalendarev R I, Sazonov A I, Rodionov A N, Chikvaidze G V and Eiduss J A 1983 *Mater. Res. Bull.* **19** 11
- [5] Rodionov A N, Kalendarev R I, Chikvaidze G V and Eiduss J A 1979 *Nature* **281** 60
- [6] Corbridge D E 1974 *The Structural Chemistry of Phosphorus* (Amsterdam: Elsevier)
- [7] Daniel M F and Leadbetter A J 1981 *Phil. Mag.* **B 44** 509
- [8] Rodionov A N, Kalendarev R I, Shendrik A V and Zakis Yu R 1983 *Phys. Status Solidi* **a 79** K151
- [9] Woodward R B and Hoffmann R 1970 *The Conservation of Orbital Symmetry* (Weinheim)
- [10] Rodionov A N, Kalendarev R I and Shendrik A V 1983 *Phys. Status Solidi* **a 74** K155
- [11] Taylor P S, Friebele E J and Bishop S G 1978 *Solid State Commun.* **28** 247
- [12] Eiduss J, Chikvaidze G, Kalendarev R, Rodionov A and Sazonov A 1995 *J. Mol. Struct.* **348** 123
- [13] Sazonov A I and Kalendarev R I 1983 *Latvian J. Phys. Tech. Sci.* **3** 26
- [14] Gillespie R I 1972 *Molecular Geometry* (London: Van Nostrand Reinhold)
- [15] Rodionov A N and Kalendarev R I 1983 *Latvian J. Phys. Tech. Sci.* **1** 111
- [16] Haser M, Schneider U and Ahlrichs R 1992 *J. Am. Chem. Soc.* **114** 9551
- [17] Jones R O and Hohl D 1990 *J. Chem. Phys.* **92** 6710
- [18] Martin T P 1986 *Z. Phys.* **D 3** 211
- [19] Jones R O and Seifert G 1992 *J. Chem. Phys.* **96** 7564
- [20] Morino Y, Ukayai T and Ito T 1966 *Bull. Chem. Soc. Japan* **39** 64
- [21] Ahlrichs R, Brode S and Ehrhardt C 1985 *J. Am. Chem. Soc.* **107** 7260
- [22] Yang C Y, Paesler M A and Sayers D E 1987 *Phys. Rev.* **B 36** 980