

Formation of As₈ dimers in molecular solid-state arsenic

A.N. Rodionov^{1,a}, Yu.F. Zhukovskii^a, R.I. Kalendarev^{a,*}, J.A. Eiduss^b

^a*Institute of Solid State Physics, Kengaraga 8, Riga, LV-1063, Latvia*

^b*University of Latvia, Rainis boulev. 19, Riga, LV-1098, Latvia*

Received 26 August 1996; accepted 6 September 1996

Abstract

Molecular yellow arsenic (y-As) consists of tetrahedral As₄ molecules that may be packed in various ways. All y-As modifications, both disordered and crystalline, are metastable and undergo irreversible transitions (polymerization) under action of heat and light, which cause a change in the nature of bonding in the molecules. Polymerization of y-As leads to the formation of amorphous arsenic (a-As) possessing a continuous random network structure. DTA studies show that polymerization is an activated exothermic process. The value of its enthalpy agrees satisfactorily with an estimate of the excess energy of strained 'banana-shaped' bonds in an As₄ molecule.

Quantum chemical calculations, applying the semiempirical CNDO/BW approach, show that at the initial polymerization stage we have a formation of As₈ dimers due to cleavage of one bond in the tetrahedral As₄ molecule. Simulation of this process shows that formation of a stable As₈ cluster, possessing either D_{2h} or O_h symmetry, may take place if the dimerization reaction path possesses D_{2d} symmetry. In this case a pair of approaching molecules is positioned in staggered 'face-to-face' configuration, which may be considered as a conformation with a six-membered chair-shaped ring dominating in the structure of polymerized a-As. The most favourable is found to be a molecular As₈ dimer with eclipsed 'edge-to-edge' configuration (D_{2h} symmetry). © 1997 Elsevier Science B.V.

Keywords: As₄ molecule; Yellow arsenic; Polymerization; DTA; CNDO/BW

1. Introduction

Owing to an s^2p^3 electron configuration in the valence shell, arsenic is capable of forming three σ -bonds positioned in an orthogonal arrangement which determines the possibility of forming tetrahedral molecules of As₄ [1]. Condensation of As₄ vapour on substrates below 200 K produces arsenic as a molecular solid consisting of tetrahedral As₄ molecules that may exist in several crystalline and amorphous

states. This is the yellow modification of arsenic (y-As). It reveals photosensitivity over a wide spectral range. Under the effects of illumination (visible region), irradiation (UV, X-rays, particles) and on heating, irreversible changes take place in the molecular structure of y-As, bond switching between the As₄ molecules, with formation of a molecular covalently bonded network of amorphous arsenic (a-As). These structural changes constitute the basis of the practically important image formation on y-As layers [1]. However, unlike other allotropic forms of solid arsenic, existing data about y-As are, so far, extremely poor [2,3].

* Corresponding author.

¹ Deceased

The polymerization of γ -As under the above-mentioned effects is a multistage process. The starting stage of molecular cluster formation is of particular interest, namely 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 differ depending on molecular packing in different γ -As modifications. However, 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 [3]. As a result of the reaction, we observe cleavage and switching of bonds between the As_4 molecules, with formation of intermediate molecular clusters. Molecules from the nearest surroundings may also be involved in this process, leading to the creation of the neighbouring phase, which is thermodynamically more stable, in the bulk of γ -As [4].

Recently, we have studied experimentally and theoretically various molecular modifications of γ -As and their structural transformations [1,5–7]. In the present work both DTA measurements of pure yellow arsenic and CNDO/BW quantum chemical calculations of different stable As_8 configurations, as well as possible transition pathways between them, have been continued for further elucidation of the mechanism of γ -As polymerization.

2. Method details

2.1. DTA measurements

The existence of various allotropic forms of yellow arsenic suggested an investigation of the thermodynamics of the process. For this purpose a special differential microcalorimeter of the Calvet type was constructed [8] and adapted for investigating heat phenomena in thin deposited layers at low temperatures. Our DTA device had a maximum sensitivity of $6 \mu W$ with respect to heat emission within the 90–420 K range. All the measurements were carried out at a heating rate of $1 K min^{-1}$. Yellow arsenic layers were deposited in a separate vacuum cryostat ($\sim 10^{-5}$ torr) in the dark. A more detailed description of our DTA experiments was given earlier [4–6].

The γ -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 released in exo- and endo-processes must be in proportional dependence on the mass of the sample. Crack formation on γ -As films could sometimes be observed at temperatures exceeding 280 K in the form of 'noise' on the declining part of the exothermic DTA curve. The films started to show cracks in the transition process after more than half of the sample had polymerized.

Irradiation of the γ -As layers obtained was carried out inside the cryostat in nitrogen atmosphere. For this purpose an X-ray tube with a Cu anode was used, for the K_α radiation of which the layer thickness for half attenuation exceeds $30 \mu m$. Such radiation interacts with the layer material uniformly throughout the whole bulk. Illumination of the γ -As samples by strongly absorbed light with $\sim 2.5 eV$ photon energy was effected in the process of their preparation. 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% $CuSO_4$ solution. The total illumination dose exceeded by several orders of magnitude the value necessary for producing a photographic effect in γ -As [6].

2.2. CNDO/BW calculations

Details of the semiempirical study of equilibrium molecular clusters of arsenic have been recently described by us elsewhere [7]. All the calculations were performed for the singlet states of various As_8 cluster configurations in *sp* basis of the valence electrons. The following scheme of quantum chemical modelling is foreseen in our original version of CNDO/BW code:

- preliminary calibration of two-centre α_{XY} and β_{XY} parameters for the corresponding X–Y bond within the small test molecules according to their equilibrium geometry and binding energy;
- optimization of both possible structures of the system under study and transition trajectories between them, using semiempirical calculations of the total energy for successively

varying geometry of this system according to the method of cyclic coordinate descent;

- simulation of various types of intramolecular vibration for the equilibrium structures, using the synchronous scanning of a number of independent internal coordinates.

We used the z axis passing through the outermost atoms of a pair of remote tetrahedral As_4 molecules positioned with respect to each other along the z direction according to D_{3d} symmetry as the basic dimerization reaction pathway. We optimized independently five to seven pairs of internal coordinates (synchronously for both As_4 molecules) in the course of approach of the two interacting molecules along this pathway. As a result of pathway optimization, the binding energy curve $-E_{\text{bind}}(z)$ was calculated. In addition to the one-dimensional scanning along the z coordinate, a similar procedure of two-dimensional scanning along a pair of coordinates was performed. Such a simulation allowed us to calculate various energy surfaces, for instance $-E_{\text{bind}}(z, \theta)$, which are more suitable for theoretical simulation of the reaction pathways.

3. Results and discussion

Our DTA measurements reveal two singularities for freshly prepared γ -As layers: an endothermic heat effect at 227 K (due to a reversible transition into the plastic phase characterized by a disordered orientation of the As_4 molecules through rotation around the z axis) and an irreversible exothermic effect with maximum heat release at 280 K (due to polymerization of the molecular arsenic). The applied X-ray dose produced structural changes in about 5% of the material, which distributed themselves uniformly throughout its bulk. Irradiation leads to a shift of the exothermic peak by ~ 10 K towards lower temperatures. The position of the endothermic peak remains practically unchanged, whilst the process itself proceeds against the background of additional heat release. In the case of sample illumination, heat release is still more marked, when part of the polymerized amorphous phase becomes comparable with the amount of the initial γ -As. Intensities of the exo- and endothermic peaks of γ -As allowed us to

estimate its content as 30%. The peak of the polymerization exotherm also shifts towards lower temperatures. The relative stability of γ -As at low temperatures is determined by the existence of an energy barrier. According to the kinetic equation of Avrami [9] its height was found to be 0.48 ± 0.07 eV.

We consider polymerization to be due to the relatively low stability of the tetrahedral molecules of As_4 owing to 'banana'-type strained bonds. This is a result of the s^2p^3 electron configuration possessing characteristic $p\sigma$ -bond angles exceeding 90° . The excess energy of strain of the molecular tetrahedron is removed in the process of bond cleavage and switching between the interacting As_4 molecules. This results in a change in the type of structure elements: the tetrahedral molecules of As_4 disappear, and instead we observe an appearance of trigonal pyramid-shaped structure units $AsAs_3$, with different bonding angles and lengths.

Such an interpretation is confirmed by our CNDO/BW calculations. Careful geometry optimization indicates the existence of the following equilibrium configurations of the As_8 cluster:

1. a pair of remote tetrahedral As_4 molecules (asymptotic plane on the energy hypersurface);
2. a staggered 'face-to-face' configuration possessing D_{2d} symmetry (the corresponding local minimum on the hypersurface is higher by 183 kJ mol^{-1} with respect to the $2As_4$ configuration);
3. a cubane (cube-like) configuration possessing O_h symmetry (its local minimum is lower by only 14 kJ mol^{-1} than the above-mentioned asymptotic plane on the hypersurface); as for stability of the cubic configuration, it is probably due to disregard of the repulsive effect of parallel bonds;
4. an eclipsed 'edge-to-edge' configuration possessing D_{2h} symmetry (its minimum is the deepest among the configurations considered, lying 35 kJ mol^{-1} lower than an asymptotic plane).

The z axis is a basic pathway for the structural transitions $1 \rightarrow 2 \rightarrow 3$ within the framework of D_{2d} symmetry trajectory. Both cleavage and switching of a pair of nearest As-As bonds takes place for the dimerization reaction $1 \rightarrow 2$. As for the transition pathway $2 \rightarrow 4$, it is characterized by a more complicated trajectory. All the transitions are found to be low-activated processes.

References

- [1] J. Eiduss, R. Kalendarev, A. Rodionov, A. Sazonov, and G. Chikvaizde, *Phys. Stat. Sol. (b)*, 193 (1996) 3.
- [2] G. Linck, *Ber. Dtsch. Chem. Ges.*, 32 (1899) 888; 33 (1900) 2284.
- [3] M.F. Daniel and A.J. Leadbetter, *Phil. Mag. B*, 44 (1981) 509.
- [4] A. Rodionov, R. Kalendarev, A. Shendrik and Yu. Zakis, *Phys. Stat. Sol. (a)*, 79 (1983) K151.
- [5] J. Eiduss, G. Chikvaizde, R. Kalendarev, A. Rodionov and A. Sazonov, *J. Mol. Struct.*, 348 (1995) 123.
- [6] A. Rodionov, R. Kalendarev and J. Eiduss, *J. Phys.: Condens. Matter* 7 (1995) 5805.
- [7] A. Rodionov, R. Kalendarev, J. Eiduss and Yu. Zhukovskii, *J. Mol. Struct.* 380 (1996) 257.
- [8] A. Rodionov, R. Kalendarev, G. Chikvaizde and J. Eiduss, *Nature*, 281 (1979) 60.
- [9] G.N. Greaves, S.R. Elliot and E.A. Davis, *Adv. Phys.*, 28 (1979) 49.