Mechanism of photoinduced optical effects in amorphous As$_2$S$_3$

Part II. Reversible changes of optical properties

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Mechanism of photoinduced structural transformations in amorphous As$_2$S$_3$ is studied with differential IR Fourier-spectroscopy technique in the 400 − 100 cm^{-1} region. Stage of reversible photodarkening is realised in a-As$_2$S$_3$ samples after first cycle of photoexposure and annealing. The corresponding destruction-polymerisation reaction is opposite to the one obtained for irreversible changes. The whole scheme of photo- and thermoinduced structural transformations in a-As$_2$S$_3$ is presented as multicyclic process of coordination defect formation and annihilation. The vibrational density of states calculated using quantum solid state methods supports additionally the presented experimental results and their interpretation.

1. Introduction

The reversible photoinduced optical effects in amorphous As$_2$S$_3$ layers obtained by thermal vacuum deposition reveal themselves through changes in the physical properties during second, and all following cycles of photo-exposure and annealing at temperature near the glass transition point [1, 2]. These effects have been well studied in 1970–1980, but now there is a diversity of viewpoints concerning our understanding of their microstructural mechanism. Moreover, existing models describing the nature of reversible photoinduced effects in amorphous chalcogenide semiconductors (AChS) have semi-empirical character. The following models can be distinguished at present:
− the photodecomposition model [3],
− the model of non-equilibrium distribution of occupied carriers [1],
− the photostructural transformations (PhST) model [2, 4, 5],
− the homopolar intramolecular bond-breaking model [6],
− the model of charged deep defects [7],
− the local heating model [8],
− the model of quasimolecular defect centres [9],
− the heteropolar intramolecular bond-breaking model or the random covalent network transformations model [10],
− the intermolecular bond-breaking model [11],
− the model of local phase transitions [12].

Such a situation is obviously caused by difficulties in the direct observation of local atomic structure transformations in disordered solids (AChS in particular) using "traditional" amorphographical technique. The reversible photoinduced changes are very weak as they include no

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Opto-Electr. Rev., 4, N°1/2, 1996

O.I. Shpotyuk, J. Kasperczyk, S. Szymura and I. Kityk   69

more than 10% of the atomic nodes concentration, and the sensitivities of the corresponding oscillating modes in absorbed vibrational spectra are low. Optical spectroscopy methods containing useful information in integral signal are less informative for this purpose. Necessary information on the PhST can be accurately obtained from differential Fourier-spectroscopy technique in long-wave IR region (400−100 cm⁻¹).

For the first time this technique was applied to amorphous As_2S_3 in 1988 [13]. The main aim of that experiment − the identification of irreversible short-range order PhST induced by absorbed light beam − was successfully achieved for a-As_2S_3 thin films. However, it is expected that differential IR Fourier-spectroscopy technique will be also quite informative for studies on the mechanism of reversible PhST in AChS. In addition, the experimental data on photoinduced changes of AChS intermediate- range order structure obtained earlier using EXAFS-spectroscopy method [11, 14] must be taken into account for the formation of unified model of reversible PhST on the level of both short- and intermediate-range orders.

Thin layers of a-As_2S_3 2−2,5 µm thick, investigated in this paper were obtained by vacuum evaporation, as was described previously [13]. Photoexposure of thin films was carried out by unfocused laser beam (442 nm) absorbed at power density P = 25 mWcm⁻² during 120 min. The temperature of annealing was T = 423 K and its duration was 30 min. The conditions of IR Fourier-spectroscopy experiments were presented in papers [13] and [15]. It must be noted that the a-As_2S_3 vibrational spectrum contains the bands: 335−285 cm⁻¹ (pyramidal AsS_3 units); 379, 340, 231, 210, 168 cm⁻¹ (molecular products with "wrong" homopolar As-As bonds); 243, 188 cm⁻¹ (molecular products with "wrong" homopolar S-S bonds) [18-21]. An uncertainty of the above presented vibrational spectra is especially connected with the 340 cm⁻¹ band, according to experimental results obtained for the a-As_2S_3 with the high pyramidal AsS_3 units concentration [18,19].

2. Experimental results

Spectral distributions of the additional optical density ΔD of a-As_2S_3 induced by third cycle

photoexposure (a) and annealing (b) are illustrated in Fig. 1. Absorbed light beam increases the vibrational modes intensities of structural complexes with homopolar As-As (379, 340, 231, 210 and 168 cm⁻¹) and S-S bonds (243 and 188 cm⁻¹), while concentration of pyramidal AsS_3 and bridge As-S-As units containing heteropolar As-S chemical bonds (335-285 cm⁻¹) is decreasing during the experiment. The full process of reversible PhST in a-As_2S_3 may be presented by the following destruction-polymerisation reaction

$$(As-S) \rightarrow (As-As) + (S-S), \qquad (1)$$
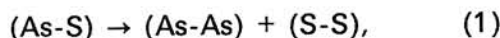
where expressions in brackets denote chemical bonds destroyed or formed in result of photoexposure. The following annealing of investigated samples is fully reversible (see Fig. 1b). In multiple photoexposure-annealing cycles these changes of
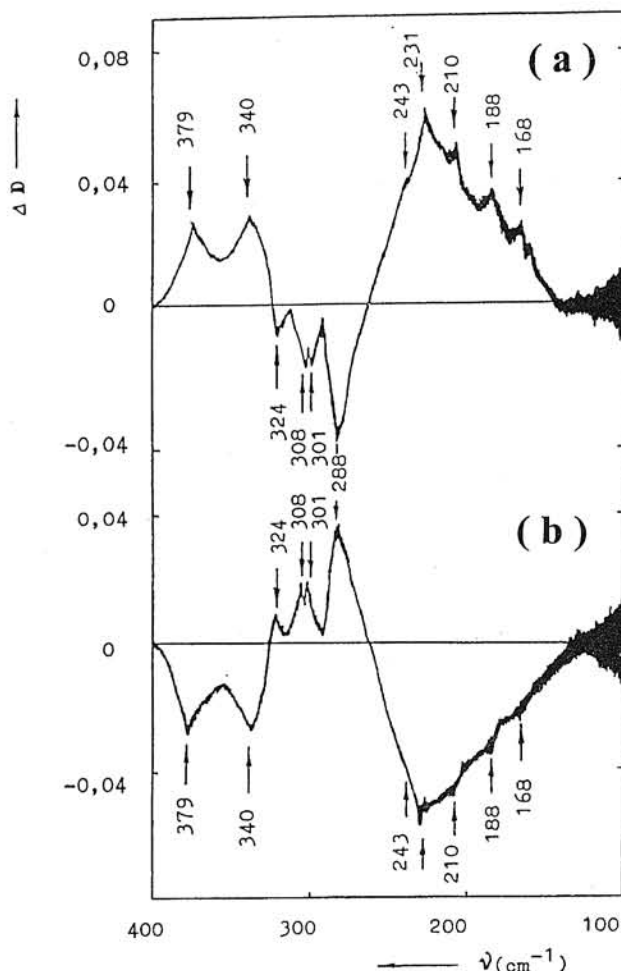

Fig. 1. *Additional optical density in a-As_2S_3 thin film induced by third cycle of photoexposure (a) and annealing (b).*

optical density ΔD may be repeated with small irreversible component (2−3%). It should be noted that 231 cm^{-1} vibrational mode sensitivity (first of all) to intermolecular PhST [21] is the most intensive in the obtained spectra. The same result was received earlier by Frumar et al. [10].

Thus, the structural character of reversible photoinduced effects in a-As$_2$S$_3$ is certainly proved. Quantitative analysis shows that no more than 6−7% of atomic nodes take place in observed processes what agrees well with the results obtained by Raman spectroscopy [10]. Moreover, while the authors of [10] conclude about destruction-polymerisation reaction due to 231 cm^{-1} vibrational mode changes, our results indicate the initial (heteropolar chemical bonds) and final (homopolar chemical bonds) products of reversible PhST.

3. Mechanism of reversible optical effects

3.1. Channel of reversible PhST

Let's consider all possible variants of photoinduced coordination defects formation (CDF) [5,15] in a-As$_2$S$_3$ described by reaction (1). Eight D^+, D^- − defects generation schemes accompanied by the destruction of heteropolar chemical bonds (see Fig. 2) must be stood in the centre of this analysis. Schemes N 5−8 can be excluded from consideration since they don't change bonds types. Schemes N3 and 4 perhaps are characteristic of non-stoichiometric chalcogen- and arsenic-rich AChS. Thus, reversible photodarkening of a-As$_2$S$_3$ thin films are connected with (As$^-_2$; S$^+_3$) and (As$^+_4$; S$^-_1$) defects formation due to schemes (1) and (2) in Fig. 2 (upper index in the defect signature means charge state and lower one − coordination number).

Annealing displaces equilibrium of these schemes into opposite state, and non-defect initial state of a-As$_2$S$_3$ samples restores. Speaking in another way, probabilities of defect annihilation and heteropolar (As-S) bonds occurrence in a-As$_2$S$_3$ increase at high temperature.

Taking into account experimental results on irreversible stage of PhST [13,15] the complete topological scheme of reversible effects in a-As$_2$S$_3$ thin films may be presented as united process of destruction-polymerisation transformations shown in Fig. 3.

3.2. Efficiency of PhST

In spite of similarity between final products in reversible PhST (see Fig. 3) and D^+,D^- − centres of the self-trapped exciton model [5], some additional remarks should be formulated regarding microstructural defect formation mechanism in a-As$_2$S$_3$. In fact, if we will take into account only qualitative atomic configuration characteristics (chemical bonds type, mainly) for one or another structural state (for example, state 3 in Fig. 3), then it will be difficult to explain why the transformed bonds concentration is less than 6−7%. Usually, factors determining defect formation efficiency are not considered in the self-trapped exciton model. So, coordination defects represent quasiatomic centres which contain excess electrical charge and are characterised by negative electron correlation energy. Strong polaron effect in this model appears due to the interaction between empty-occupied positive centres and lone-pair electrons of neighbouring atom (donor-acceptor interaction). Only a qualitative analysis of atomic and molecular orbitals energies is taken into account.

In CDF model, reversible PhST are considered as interconnected processes of chemical bonds switching (short-range order changes) and following relaxation transformations (intermediate-range order changes) including large space a-As$_2$S$_3$ network (3−5 coordination spheres that is near 10^3 Å^3). As it was shown in Fig. 3, all atomic nodes taking part in reversible PhST (pyramidal AsS$_3$ complexes) are formed in such nets of structural matrix where originally homopolar bonds existed (compare state 1 and 3). Local atomic density of changed structural blocks is approximately less than average AChS density because homopolar bonds are more extended than heteropolar are [22, 23]. It means that force constants of reversibly transformed complexes, first of all, intermolecular AsS$_3$−AsS$_3$ interaction constants, are reduced in comparison to these which concern complexes in other sides of a-As$_2$S$_3$ structural matrix. Therefore, these comp-
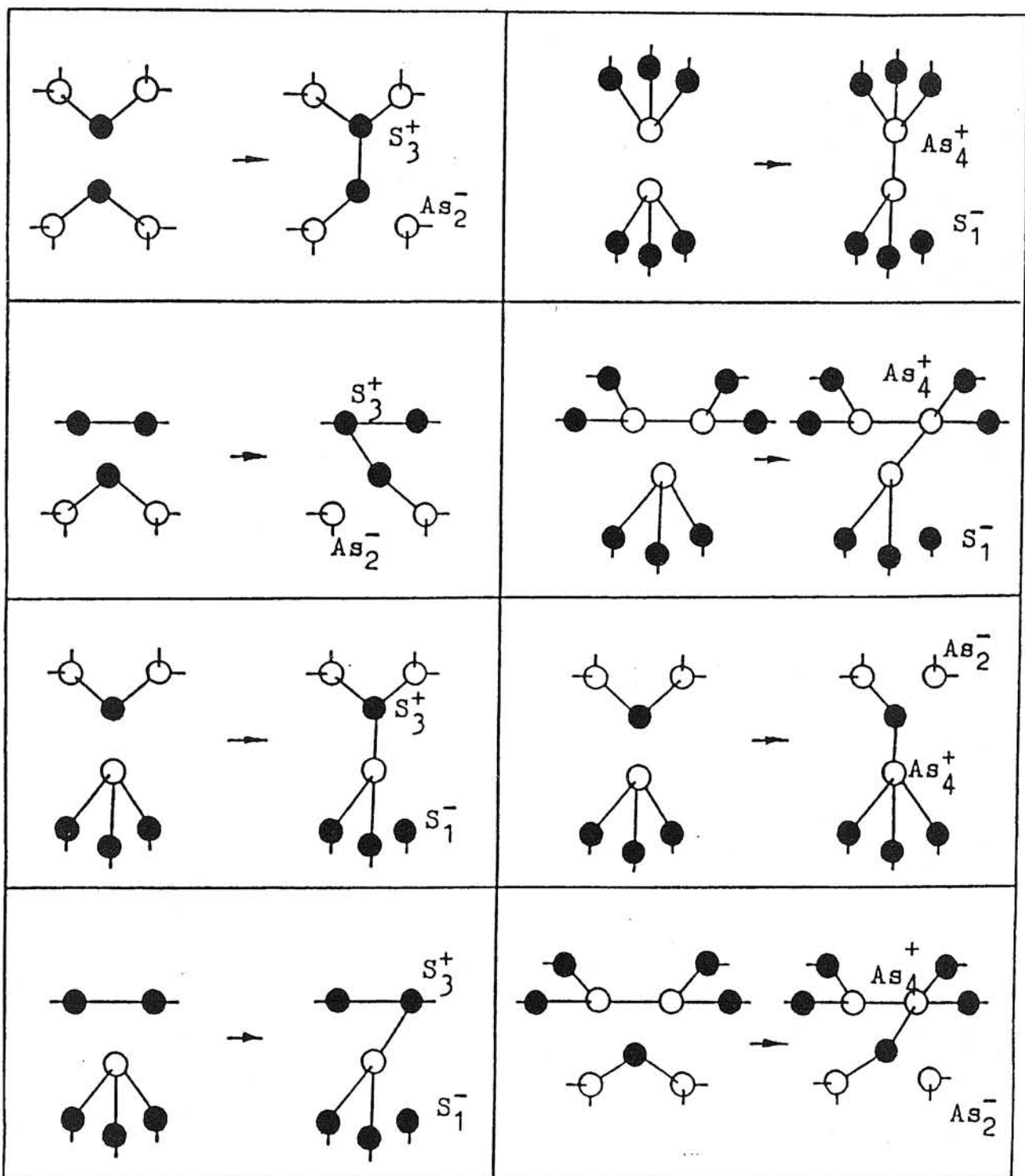
Fig. 2. Defect formation in a-As₂S₃ accompanied by heteropolar bond-breaking transformations.

lexes can be classified as soft atomic configurations having double-well potential and negative electron correlation energy [24, 25]. Concentration coincidence of reversibly transformed bonds and soft atomic configurations is an additional confirmation of this assumption.

Network rigidity and relaxation effects in the nearest neighbourhood of appearing coordination
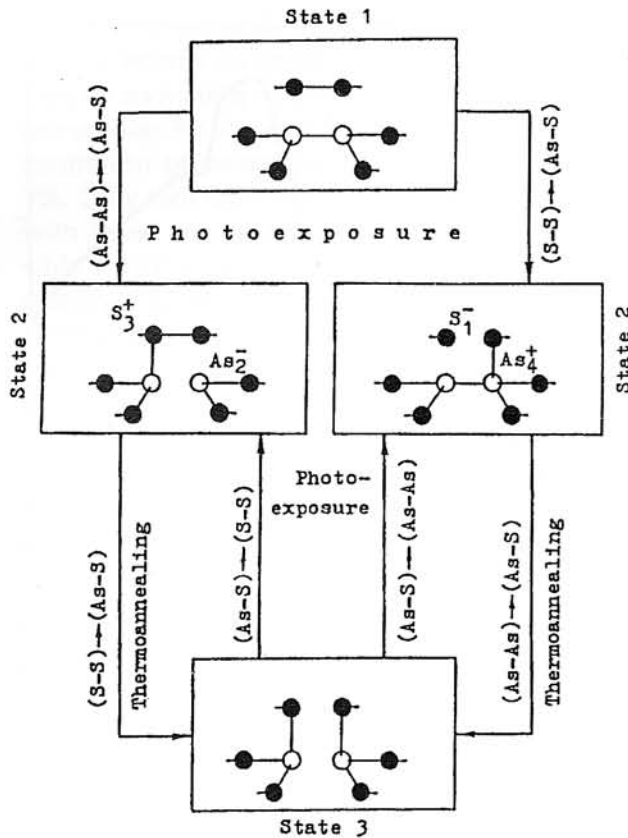
Fig. 3.Topological scheme of reversible photostructural changes in a-As₂S₃.

centres are accepted in CDF model as main decisive factors. Their quantitative characteristic is given by local atomic density δ [26]:

$$\delta = \rho \left(\sigma \sum \frac{A_i x_i}{\rho_i} - \frac{\sum A_i x_i}{\rho} \right) / \sum A_i x_i \qquad (2)$$

where A_i, x_i and ρ_i are atomic mass, atomic weight and density of the i-structural fragment after bond switching, ρ − average density of sample. Reversible PhST are more effective in AChS with small local atomic density δ. Hence photoinduced changes of optical properties increase in the sample row "bulk-powder- thin film" in good agreement with well-known experimental data [11].

The existence of AChS photoinduced state is conveniently connected with defect pairs stability. Let's introduce a parameter which is equal to the difference of bonds dissociation energies before and after photoexposure. If $(As^-_2; S^+_3)$ − pairs concentration will be denoted x_1 and $(As^+_4; S^-_1)$

− pairs concentration − x_2, then energetic activation barrier of reversible PhST in a-As₂S₃ can be written in the following way:

$$\Delta E = \frac{\varepsilon_1 x_1 + \varepsilon_2 x_2}{x_1 + x_2} \qquad (3)$$

Supposing that both of the reversible PhST channels are equally possible ($x_1 = x_2$), ΔE values can be calculated for AChS films: As₂S₃ (20 kJ/mol.), As₂Se₃ (17.5 kJ/mol.) and As₂Te₃ (7.5 kJ/mol.). Photoinduced changes also decrease in such consistency [11]. Photodarkening efficiency in non-stoichiometric AChS can be estimated taking into account the difference of ε_i value for various schemes of CDF.

3.3. Microstructural model of reversible PhST (CDF model)

Taking into account our experimental results (Figs. 1−3), the main features of earlier proposed soft atomic configuration [24, 25] and the unified intra- and intermolecular bond-breaking models [11] we can present the mechanism of reversible PhST in a-As₂S₃ by the following photoinduced stages:
1. Excitation of electron or (and) hole pairs auto-localised at soft atomic configurations (as initial microscopic process).
2. Weakening of inter-molecular bonds resulting in possibilities of atomic groups displacements.
3. Metastable state formation due to structural changes at the short-range (chemical bonds redistribution or CDF) and intermediate-range order levels (rearrangements of atomic blocks, displacements of non-bonded atoms).

These stages are interconnected and depend not only on chemical-technological peculiarities of investigated thin films, but also on temperature and spectral distribution of absorbed light.

Thus, intra- and intermolecular bond-breaking processes are involved in the model of reversible PhST in a-As₂S₃ as described by S.R. Elliott [11]. The real scheme of bonds switching associated with photodarkening (Fig. 3) can be received considering all possibilities of local coordination changes. This approach, unfortunately, was not accounted for in the paper [11] as only four kinds

of D^+, D^- – defect formations in As_2S_3 amorphous matrix were discussed there.

3.4. Quantum chemistry modelling of PhST

We have performed theoretical calculations to confirm our experimental results and their interpretations shown in Fig. 2 and Fig. 3. To estimate a density of quantum states we have investigated electron states and proper optical transitions for the As-S clusters before and after the photoinduced processes (see the structural fragments in Fig. 3). The 3s, 3p states of S and 3s, 3p states of As were taken into consideration.

The electronic structure has been calculated self-consistently using a standard Linear Muffin Tin Orbitals (LMTO) technique in an atomic sphere approximation [27]. Necessary quasi-Brillouin zone integrations have been performed using a linear tetrahedron technique based on a grid of 80 k-points in the irreducible part of the quasi-Brillouin zone. The LMTO Hamiltonian was transformed into a tight-binding form for higher order approximations. The two-centre tight binding Hamiltonian in the Lowdin orthogonal representation was applied in the form described in [28].

The evaluations of the optical function I(E) were performed for the structural states 2 and 3 (Fig. 3) of the a-As_2S_3 system using a standard computer program package Hypcd-4. The calculated result for the spectral dependence of the differential optical function $\Delta D(v)$ is presented in Fig. 4 depending on the wave number v for the stage of the reversible photodarkening. We have assumed that the state 2 (in Fig. 3) was a superposition of two defect states.

It is necessary to notice that the theoretical results are in a quite good agreement with the experimental curve shown in Fig.1a what gives a strong evidence for a general validity of our assumptions concerning the initial bond structures and the final ones arising in the result of the above mentioned structural transformations.

However, there are few differences between the calculated and the experimental dependences, that are listed below.

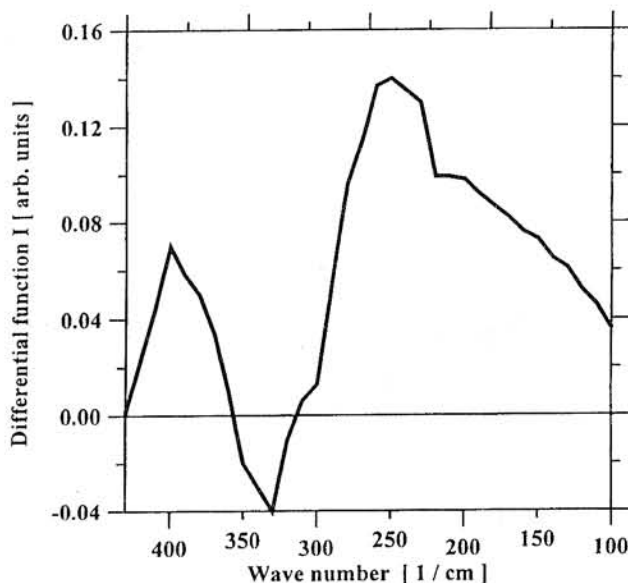1) Chosen intensities of the vibrations associated with the heteropolar As-S bonds are shifted

Fig. 4. Calculated results for differential optical function depending on a wave number v (in cm⁻¹)

towards the 340 cm⁻¹ vibrational band (it is interesting to note that the positive experimental change ΔD in the spectral range lies in the vicinity of the 335−285 cm⁻¹ bands).

2) A sharp minimum of the differential signal is observed in the 335−285 cm⁻¹ range although its intensity is still positive because of a superposition with the additional positive contribution for $v < 275$ cm⁻¹.

3) The low frequency bending mode of the a-As_2S_3 spectrum is also shifted a bit from the 270−150 cm⁻¹ range towards the short wavelength that is most probably caused by its much higher sensitivity to the changes of the intermediate-range bond ordering. This was unfortunately not included in our theoretical considerations.

It can not be excluded that relaxation processes around the coordination defects (for the intermediate-range ordering experimentally detected by an EXAFS method [14]) could be a reason of such a behaviour of the differential optical function $\Delta D(v)$ in the spectral range between 335 and 285 cm⁻¹.

4. Conclusions

Reversible PhST observed in second and following cycles of absorbed light photoexposure

(first cycle includes photoexposure and annealing of freshly-evaporated films) are accompanied by switching of heteropolar As-S bonds into homopolar As-As and S-S ones, but total concentration of switching bonds is not lager than 7%. Only two CDF processes may be associated with these transformations. Efficiency of reversible PhST in a-As_2S_3 is given by local atomic density δ [2] and energetic activation barrier ΔE [3] that allow to explain experimentally obtained concentration dependence of photoinduced effects. Reversibly transformed nets in structural AChS matrix are soft atomic configurations with negative correlation energy of carriers. Investigated photoinduced changes include not only short-range order transformations, but also intermediate-range order ones evidenced by EXAFS-spectroscopy technique [14]. The validity of the mentioned ordering transformations was additionally supported by the quantum solid state calculations of the vibrational density of states in the a-As_2S_3 system.

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