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HYBRIDIZATION MODEL OF PHOTO-INDUCED METASTABLE ATOMIC STATES IN CHALCOGENIDES

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Existing models of photo-induced metastable states in chalcogenides are reviewed. In almost all of these models the metastable states are connected with specific local environment causing the possibility of two wells for a structural unit. A model describing the appearance of metastable atomic configurations in chalcogenide glassy semiconductors has been elaborated in the present paper. In this model two-well potentials arise due to the properties of the main structural unit itself, regardless of atomic environment. Atomic potentials for this structural unit of glass are calculated using Born-Oppenheimer adiabatic approximation. Values of parameters allowing the appearance of metastable states of structural units are discussed.

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1. Introduction

There are numerous data on photo-induced phenomena in the chalcogenide glassy semiconductors (CGS). The scalar photo-induced phenomena are independent of light polarization. Among them there are irreversible changes, such as densification and photopolymerization, and reversible effects, for example, the shift of the optical absorption edge. The reversible photo-induced change of optical absorption of chalcogenide glassy semiconductors has been discovered in the early 70's [1-3]. Since that time many papers have been devoted to investigation of this phenomenon.

The detailed analysis of this phenomenon has been made in the books [4,5] and recently (in 2001) has been presented at the First International Workshop on Amorphous and Nanostructured Chalcogenides in Romania [6-11].

In the end of 70's the vectorial photo-induced phenomena have drawn attention. These are photo-induced anisotropies of electrical and optical properties. The discovery of vectorial effects was made by Zhdanov, Kolomiets, Lyubin and Malinovskii [12,13]. Lyubin and coauthors [14] have observed photo-induced anisotropy of reflection coefficient in films and bulk samples of $As_{50}Se_{50}$ and $Ge_{20}As_{20}S_{60}$. The photo-induced anisotropy of AsSe films conductivity has been studied in the paper [15]. The photo-induced anisotropy of light scattering has been reported in the paper [16].

As to the mechanism of photo-induced phenomena, Tanaka et al. [17] has revealed that there is reversible change of intensity and half width of the first diffuse peak of the diffracted X-ray intensity, which occurs simultaneously with reversible scalar phenomenon, namely – photodarkening. So the reversible photodarkening is connected with photostructural change of the main structural units of CGS, not defects. It is very possible that the latest conclusion is valid for vectorial phenomena also.

There are several models which have been suggested to explain reversible photostructural changes [18-21]. According to Kolobov and Adriaenssens [18], the reversible photostructural changes are connected with relaxation of tensions, which exist in samples of CGS.

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Tanaka [14] has considered the model in which the interaction of chalcogenide atoms A and B from different chains has been taken into account. During photon absorption the creation of exciton is accompanied with replacing of weak Van der Waals interaction by a strong coulombic one and, consequently, the atom A moves towards the atom B. The concept of self-trapped exciton has been considered in the paper [15].

Almost all above-mentioned models have considered two atomic positions, which are determined by the nearest environment.

The vectorial reversible photoinduced transformations have been discussed in the papers [22-24]. Grigorovici et al. [22] proposed the two stages model for these phenomenon. According to [17] the first stage for scalar and vectorial effects is the same. In the vectorial case, oppositely to scalar one, the second stage leads to a preferential orientation of covalent bonds due to the directional character of the interaction between valence alternation pairs dipole and electric field of the light wave. Lyubin and Klebanov [23] discussed the mechanisms which are different for the cases of excitation in different spectral ranges. According to Popescu [24] the vectorial effects may be explained by existence of assembly of domains which can be partially oriented by elementary bond breaking and rebonding processes.

2. Model

A model describing the appearance of metastable atomic configurations in chalcogenide glassy semiconductors has been elaborated in the present paper. In this model two-well potentials arise due to the properties of the structural unit itself, regardless of occasional atomic environment.

In our model the actual atomic coordinate is the angle between bonds of chalcogenide atom and the actual atomic unit is the basic unit C_2^0. The taking into account LP electrons of C_2^0 units is a very important feature of our model. Then two-well potentials with very slightly differentiating atomic coordinates of minima have been obtained.

Let us consider the simplest CGS, namely a-Se (Fig. 1). The hybridized wave functions and the energies of these states can be written in the following form:

$$\psi_\mu = (s + \mu p_\mu)/(1 + \mu^2)^{0,5} \tag{1}$$

$$\varepsilon_\mu = (E_s + \mu^2 E_p)/(1 + \mu^2) \tag{1a}$$

$$\psi_{LP} = p_z \tag{2}$$

$$E_{LP} = E_p \tag{2a}$$

$$\psi_{\lambda 1,2} = (s + \lambda p_{1,2})/(1 + \lambda^2)^{0,5} \tag{3}$$

$$\varepsilon_\lambda = (\varepsilon_s + \lambda^2 \varepsilon_p)/(1 + \lambda^2) \tag{3a}$$

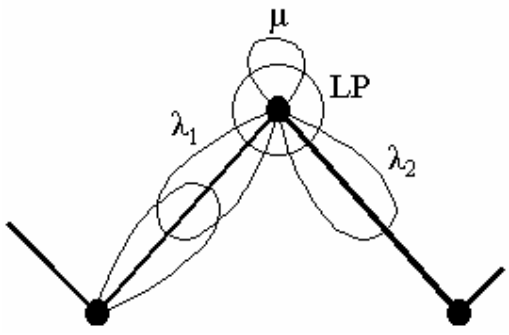


Fig. 1. The hybridized wave functions of selenium.

where $p_{1,2}$ are the linear combinations of the atomic states p_x and p_y directed to the nearest neighbors. (E_s, s) and (E_p, p) are the energies and wave functions of 4s and 4p electrons of Se. The overlapping of two ψ_λ wave functions centered on the neighboring atoms, results in splitting of E_λ to bonding E_σ and antibonding E_{σ^*} states with the following energies:

$$E_{\sigma^*,\sigma} = E_\lambda \pm VI \tag{4}$$

where we have supposed that the matrix element of hamiltonian can be presented as a product of constant V and overlapping integral I. All coefficients in the hybridizated wave functions (1-3) depend on angle φ between two bonds with the nearest neighbors due to requirement of ortogonality [25].

$$\langle\psi_{\lambda 1}, \psi_{\lambda 2}\rangle = 0 \quad \rightarrow \quad 1 + \lambda^2 \mathrm{Cos}\varphi = 0 \tag{5}$$

$$\langle\psi_{\mu}, \psi_{\lambda}\rangle = 0 \quad \rightarrow \quad 1 + \lambda\mu \mathrm{Cos}(180 - \varphi/2) = 0 \tag{6}$$

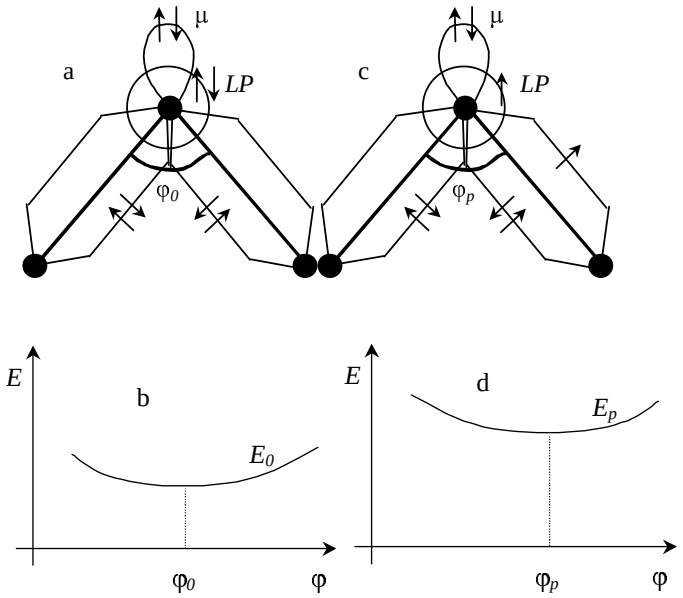


Fig. 2. The chain-like configuration of selenium. a. The basic structural unit of selenium (C_2^0) in the ground state; b. the total energy vs. bonding angle for the case a; c. the basic unit excited by a photon; d. the total energy vs. bonding angle for the case b.

Fig. 2a shows the basic structural unit C_2^0 of a chain-like selenium in the ground energy state. This state corresponds to electron configuration with two electrons with μ wave function, two LP electrons and two bonding electrons which take part in two bonds with two nearest neighbors.

So the six valence electrons of selenium are distributed as follows: two electrons occupy the hybridized state ψ_λ, two electrons are the LP electrons and two electrons participate in the two bonds with two nearest neighbors.

Fig. 2b shows the dependency of the total energy

$$E_0 = 2\,\varepsilon_\mu + 2E_{LP} + 2E_\sigma \tag{7}$$

of the basic structural unit on the angle [25], where φ_0 is the value of equilibrium angle between two bonds with the two nearest neighbors. The value of φ_0 rather well coincides with the experimental data (~103°) for value of interatomic matrix element V of order several electronvolts.

Fig. 2c shows the same basic unit, which is excited by a photon. One can see that electron goes from LP state to antibonding one. This corresponds to transition of electron from upper part of valence band to lower part of conduction band. According to [20], the value of angle that corresponds to the minimum of adiabatic potential

$$E_p = 2\varepsilon_\mu + E_{LP} + E_{\sigma^*} + 2E_\sigma \quad (8)$$

of excited basic unit is equal to 105° for the same value of interatomic matrix element V (see Fig. 2d).

The most important feature of the dependencies shown in Fig. 2b and Fig. 2d is the presence of minima in both cases, which correspond to slightly different values of the bonding angle (Fig. 3) and so to different set of hybridization coefficients in the wave functions (1-3). This is the main reason of two-well potential formation in our model. The energy difference between two minima is of order forbidden gap E_g because upper part of valence band is formed by LP states and lower part of conduction band is formed by antibonding states.

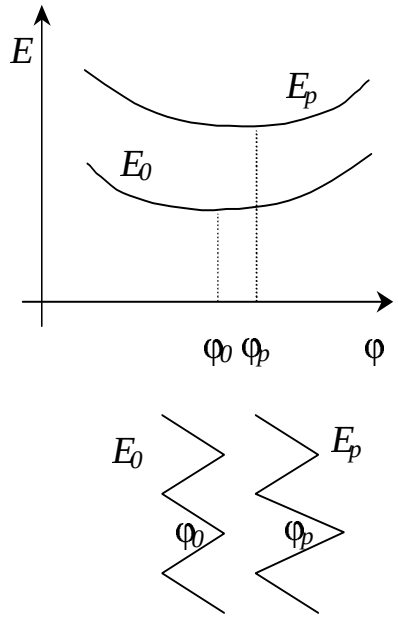


Fig. 3. The energy minima for the ground and excited state of chain-like selenium.

3. Conclusions

We have developed a model for the photostructural changes in chalcogenides glasses. These changes occur for the main structural unit of CGS and correspond to small deviation of angle between bonds for different sets of hybridization coefficients.

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