

## THE CLOSED CLUSTER MODEL AND THE CHARGED COORDINATION DEFECTS IN CHALCOGENIDE GLASSES

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A closed cluster model for the binary arsenic-chalcogen glasses seems to be attractive for the explanation of the structural and electronic properties of non-crystalline chalcogenides. In the same time the direct consequence of the model is the absence of the defects of coordination. The full implication is discussed.

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### 1. Introduction

The non-crystalline chalcogenide materials, based on chalcogens (sulfur, selenium, tellurium) offer a wealth of phenomena which are related to the reversible and irreversible changes induced by electromagnetic radiations, pressure, electrical fields, etc. [1]. The field got started by Ovshinsky who realized that the steric flexibility of chalcogenide glasses permits controlled changes in their local structure. These, in turn, result in metastable and reversible alterations of the optoelectronic and chemical properties [2,3]. These features formed the basis for various electronic switching and memory devices [4], optical memories [5] and imaging applications [6]. Ovshinsky and his collaborators pointed out the important role played by the lone-pair electrons in altering the local bonding configurations in chalcogenide glasses after excitation by light, electric fields, or by energetic particles [7]. Moreover, local-light induced structural changes result from recombination events which occur in a very small volume in these glasses because of the strong localization of the excited charge carriers [8].

In spite of tremendous effort dedicated to chalcogenide glasses the structure and properties of these materials are not completely understood [9]. Numerous papers recently published in J. Optoelectron. Adv. Materials, witness the continuous interest in chalcogenides [10-76].

The problem of the structure of simple and complex chalcogenide glasses is not yet resolved. Various models have been developed with the aim to explain the FSDP (first sharp diffraction peak) in the diffraction pattern of various non-crystalline compositions. The layer model had a certain success [77]. Nevertheless, the authors of the outrigger rafts model [78], open cluster models [79], or clustered layers model [80], failed to recognize that the problem of the boundaries of the various type of clusters is not discussed, nor the way of packing of these clusters in a detailed three-dimensional packing. What are the consequences? What is the role played by the high amount of dangling bonds, initially occurring in glass according to these models?

Many years ago there was pointed out that no ESR signal was detected in amorphous chalcogenides (a-Se, a-As<sub>2</sub>S<sub>3</sub>). This observation, i.e. the absence of spins in chalcogenide glasses, led Anderson [81] and Street and Mott [82] to formulate their negative effective correlation energy (negative-U) models, in terms of charged defects. The model allows for the presence of dangling bonds, but with the combination of positively and negatively charged dangling bonds, D<sup>+</sup> and D<sup>-</sup> having respectively no and two spin-paired electrons, being energetically favored over the neutral dangling bond D<sup>0</sup> with one unpaired electron. The defect-based version of the negative-U model was subsequently developed by Kastner, Adler and Fritzsche [83] for the case of a-Se with a singly

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coordinated, negatively charged selenium ( $C_1^-$ ) and a three-fold coordinated, positively charged site ( $C_3^+$ ) emerged as the most likely equilibrium defect configurations. Thus, the Valence Alternation Pair concept appeared.

Up to day no direct experimental evidence was found for the VAPs in chalcogenide glasses. Recently, Tanaka [84] has questioned the presence of the charged defects, on the basis of optical absorption measurements on highly purified  $As_2S_3$  samples. Adriaenssens and Stetsman [85] have reiterated the notions and consequences of the charged defects version of the native-U model and argued that even when the direct observation of the defects often fails for lack of sensitivity, there is plenty of indirect evidence for their presence in the chalcogenide glasses.

In this paper we discuss the model with closed clusters for  $As_2S(Se)_3$  and the implications on the explanation of the light induced modifications and on the balance of the charged defects (VAP) in the glasses.

## 2. Closed cluster model for binary chalcogenide glasses

Recently, we have developed a new model for the binary arsenic chalcogenide glasses. In this model the structural configurations consists in closed clusters of different extension [89].

At first, different cage-like, extended closed ends clusters and other type of clusters all without dangling bonds, based on arsenic and chalcogen atoms in stoichiometric proportions, were constructed by mounting special plastic units. Every unit simulates a sulfur (selenium) atom with two bonding directions, or arsenic atom with three bonding directions.

The coordinates of the hand-built clusters have been measured directly on the models. The coordinates and the first coordination sphere of every atom have been used as input data in a special program for the energy relaxation of the structure. In the computer array the equilibrium distance between As an S atoms was taken 0.225 nm, the bond angle on sulfur  $106^\circ$  and the bond angle on arsenic  $98.7^\circ$  (an average value) as shown by Rubinstein and Taylor [86].

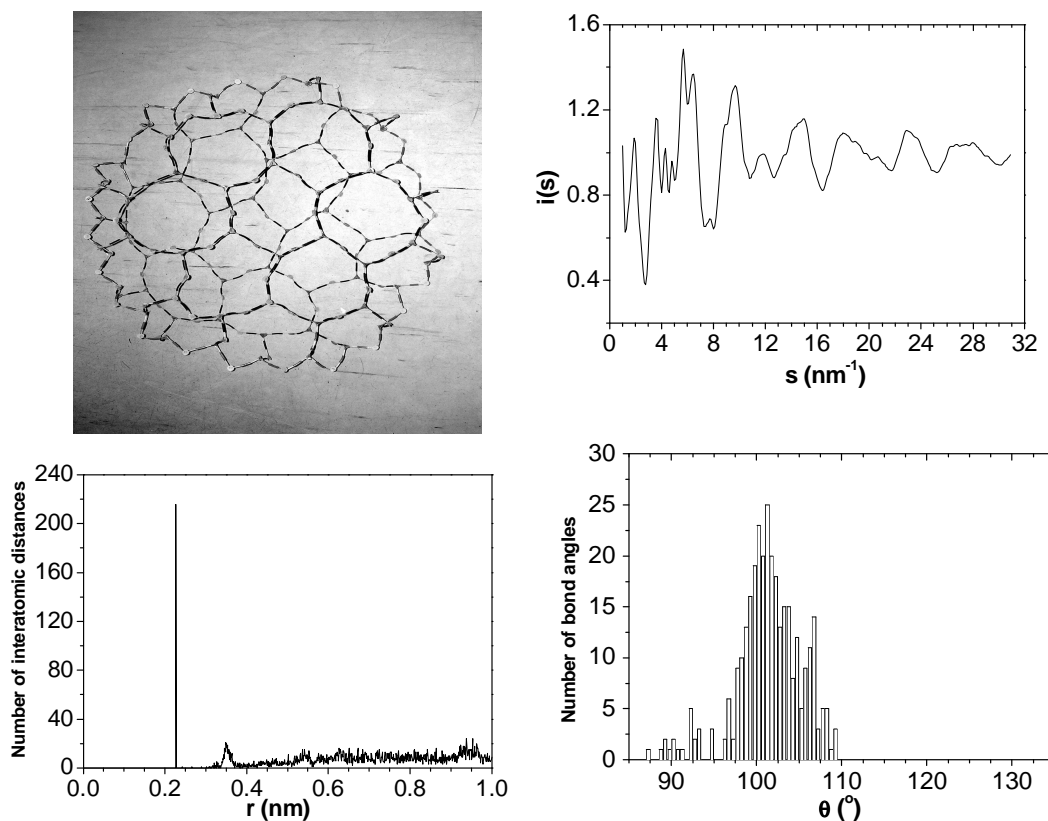


Fig. 1. The medium-size closed cluster:  $As_{72}S_{108}$ , a possible configuration in the  $As_2S_3$  glass.

The structures of minimum free energy have been calculated by an iteration procedure based on Monte Carlo – Metropolis method [87] by using the rule of minimization of the distortion energy (energy relaxation) for the whole model. The free energy was calculated with the use of the force constants taken from the literature, for the bond stretching force (As-S) and for the bond bonding force constants on arsenic and sulfur atom. The bond stretching potential centered on As-S equilibrium distance was taken as  $V_1=A(r^2-r_0^2)^2$  with  $A=2.4\times 10^{-5}$  dyn/Å<sup>3</sup> and the bond bending potential centered on the sulfur equilibrium bond angle and on the arsenic mean equilibrium angle between bonds was taken as  $V_2=B(\alpha-\alpha_0)^2$  with  $B=2.04\times 10^{-4}$  dyn.Å/rad [88].

After relaxation every model has been described by bond distance fluctuations, bond angle fluctuations, diameter and/or thickness. Structure factor and pair distribution function have been calculated. Finally the free energy per atom has been calculated and the stability of different models has been estimated according to the value of this energy.

All the families of clusters are described in [89]. An example of closed cluster is the so-called medium-size cluster in the nano-pie series. The cluster has the composition  $As_{72}S_{108}$ . After energy relaxation the structure is characterized as in Fig. 1.

The model could be extended to other low dimensional materials in the amorphous state, as e.g. amorphous arsenic. Fig. 2 shows the nano-pie structure for the first member of the series with different extension. The configuration with 26 six-fold rings of atoms and 12 five-fold rings is obtained by eliminating the sulfur atoms in the medium-size nano-pie cluster for  $As_2S(Se)_3$ .



Fig. 2. The first closed cluster in the series with planar extension (nano-pie structures) for arsenic (72 atoms).

### 3. Discussion

The new model supposes a package of closed clusters with different planar extension (different diameters), that are packed randomly in space. The agreement with the radial distribution function is rather good [89]. The first sharp diffraction peak is well reproduced due probably, to the correlation of the atoms in the parallel layers that form the closed clusters.

If the structure of e.g.  $As_2S_3$  could be understood in the terms of a random packing of medium or large size clusters, then, it is interesting to see the consequences as regarding the fundamental properties of the glass.

Firstly the anomalous increase of the FSDP with temperature observed in  $As_2S(Se)_3$  could be easily explained by decoupling the clusters and better alignment in the glass matrix.

Secondly, the lower density of the amorphous phase, compared to crystal is explained by the formation of the inherent small voids between the packed clusters.

Thirdly, the light induced phenomena (photo-expansion, photodarkening and photobleaching) could be explained.

Photo-expansion can be easily explained by light excitation of the cluster boundaries that determines an inflation of the clusters due to repelling of the planar parts.

Photodarkening must be discussed in the frame of the theory of intercluster interaction [90]. According to this theory for light-soaked effects, no bond breaking is assumed and interaction between lone-pair electrons of chalcogen atoms belonging to different clusters takes place. At the clusters boundaries there exists normal bonding sites, where the interaction between lone-pair electrons of chalcogen atoms is stronger, and accordingly, the site can act as a hole trap. When illuminated at low temperature, the photoexcited hole diffuse and are captured by the trap, then being trapped deeper through modifying the intercluster interaction. Lattice relaxation takes place. In this case, a photoexcited electron is possibly self-trapped at the excited state through deforming the structure. The trapped hole may cause the midgap absorption.

The problem of the appearance of the VAPs seems to be better understood in the closed cluster model. Initially, no dangling bonds exist, and, therefore, the amount of valence alternation pairs is strictly limited. During light excitation the cluster boundaries, in contact, will be excited so that between clusters point like charged coordination defects will appear. As a consequence small repositioning of the clusters is produced and cluster distortions will occur. The new light saturated state is darkened and expanded. By thermal annealing the initial state will be recovered (photobleaching).

One of the recently discovered phenomenon is that of photofluidity [91]. In the frame of the closed cluster model, the photofluidity could be explained by the excitation induced by light that determines the weakening of the interactions between clusters, and thus, the clusters can flow easily.

Last, but not least, the Boolchand intermediary phase observed in binary chalcogenide glasses find a simple explanation. Up to the onset of rigidity, the closed cluster formation is hindered. In  $As_x Se_{1-x}$  the onset of the intermediary phase (unstressed rigid) is at  $r_c(1) = 2.29$  and the width of the intermediate phase is 0.08 [92]. In this range the glass begins to self-organize in closed clusters. There appears, thus, two phases, a matrix enriched in chalcogen and clusters of composition  $As_2Ch_3$ . Thus the composition is nano-phase separated in the sense of Boolchand approach. For higher concentration of arsenic the composition becomes a stressed rigid phase due to interlinking of various clusters.

#### 4. Conclusions

The model with closed clusters for the chalcogenide glasses is able to give simple explanations for the whole range of light induced modifications and for the general properties of these glasses. As a consequence the dangling bonds are naturally eliminated during the glass formation, and, therefore, no significant amount of charged coordination defects is necessary to explain the glass structure. As opposite, the formation of high amount of VAPs is predicted during illumination, and in the light saturated state of the glass.

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