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Paracrystallinity or randomness: a challenge for non-crystalline structure

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The structure of low coordinated disordered materials can be understood in the frame of basically different theories: the formation of a continuous random network with all the valence bonds satisfied, the formation of small clusters (amorphites) having all the bond at the margins satisfied (closed clusters) or open clusters with many dangling bonds that are partially compensated due to the formation of valence alternation pairs, and last but not least the formation of so-called nano-paracrystalline structures, i.e. deformed nano-crystalline structures. We show that an intermediate model based on a mixture of closed and open clusters as well as layer like configurations can explain the structure and properties of the binary arsenic chalcogenide glasses.

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1. Introduction

The structure of low coordinated amorphous materials is still challenging. Among these materials, the chalcogenide glasses and thin films based on chalcogens and alloys with chalcogens are of great importance, due to interesting properties and numerous applications in optoelectronics.

The chalcogenide glasses are those glasses that contain a chalcogen (sulphur, selenium and tellurium) [1]. A high number of papers have been devoted in the last years to the simple, binary and ternary chalcogenide glasses [2 - 40]. Thin films were also largely studied [41-49] due to their applications in many devices: from photoelectric sensors till phase change memory alloys (Ovshinsky glasses) for computer memories and smart memories [50, 51]. Numerous papers recently published in Journal of Optoelectronics and Advanced Materials, witness the continuous interest in chalcogenides [52-75].

This paper discusses the main structural models developed up to day for standard chalcogenide glass (As_2Ch_3, where Ch stands for S, Se or Te) in order to elaborate a more general model that will be enough flexible to explain the main properties of the low coordinated chalcogenide glasses.

2. The structural models of non-crystalline As_2Ch_3 glass

2.1 The waved layers model

The first models of As_2S_3 glass originates from the papers written by A. Vaipolin et al., as early as 1960 [76-78]. Based on the radial distribution function of the binary arsenic chalcogenides (As_2S_3, As_2Se_3, As_2Te_3), and on the observation that the structure of an atomic layer in the crystal could be considered as a deformed layer of the close packing configuration of the chalcogen atoms linked to arsenic, Vaipolin and Porai-Koshits [76-78] proposed for the As_2S_3 a structural model, where both glass and high temperature crystalline modifications consist of atomic layers similar to those in crystal, but waved. The deformation of the layers is accompanied by the increase of the coordination number, as a consequence of the tendency to display a regular octaheder configuration. The model is supported by small coordination number of the arsenic and sulphur atoms, deduced from RDF, and by the position of the first sharp diffraction peak (FSDP) that corresponds to the diffraction line situated at 4.8 Å, given by the interference on the layer planes. Nevertheless, the model of Vaipolin et al. cannot explain the vanishing in the glass of the atomic coordination situated at 4.25 Å, characteristic to the orpiment crystal, and, moreover, cannot explain the retaining in the glass of the rigorous 6-fold rings of pyramids, typical in crystal.

It is important to compare the densities in the binary crystals and in the corresponding binary glasses. In As_2S_3 crystal the density is 3.43 g/cm^3, while in glass is 3.184 (mean value), i.e. a decrease of 7.17 %. In As_2Se_3 the density is 4.75 g/cm^3 for the crystal and 4.58 g/cm^3 for the glass, i.e. a decrease of 3.58 % when the material becomes disordered. In As_2Te_3 the density of the crystal is 6.23 g/cm^3 and that of the glass is 5.4 g/cm^3, i.e. a decrease of density of 13.32 %. Tsuchihashi and Kawamoto [79,80] explain the difference by assuming that glass, as opposite to the crystal, exhibits an “open” structure. On the other hand the FSDP in As_2S_3 defines a quasi-distance of 5.01 Å for the glass, while the corresponding (interlayer) distance in orpiment is 4.8 Å. In glassy As_2Se_3 the FSDP defines a quasi-distance of 4.93 Å, while in the crystal this distance is 4.824 Å. In glassy As_2Te_3 the quasi-distance is 4.586 Å, while the interlayer distance is 4.518 Å in crystal. Thus, the following model was proposed: the binary glass is composed of triangular pyramid As-Ch_3, bonded at the corners by the chalcogen atoms. The As-Ch_3 rings, formed by interlinking these units, are not identical. No all rings are 6-member rings. Some five-fold and seven-fold rings are integrated. Looking at the glass structure as a deformed structure, then it is easy to explain the density and the increase of the interlayer distance when one passes from crystal to glass. Due to presence of rings with different number of members, the distance of 4.25 A, characteristic to the As_2S_3 crystal, disappear in glassy As_2S_3. Similar observations can be made in the system As_2Se_3 and in As_2Te_3. In the model of Tsuchihashi and Kawamoto [80] the layers in the glass disappear due to the random orientation of the bonds between rings. Thus a three-dimensional network is formed with regions of van der Waals interactions. The fluctuations in the bonding of rings could explain the increase in the overall distance between the layers.

2.2 The paracrystalline model

In this model one looks at the structure factor of the As_2Se_3 glasses from the point of view of the micro-paracrystalline theory. The diffraction pattern of As_2Se_3 glass show peaks at the Q positions, which roughly correspond to the first and higher diffraction order of the FSDP. If these peaks can be ascribed to a single set (this hypothesis can be indeed valid for the first several peaks because for larger Q the short range order effects dominates, while the high order peaks of the main paracrystalline diffraction plane vanish) then, we can proof the relation between the peak width and the diffraction order as shown by Hindeleh and Hosemann [81]. Indeed, as Fig. 1 shows, there exists a perfect linearity between the width of the diffraction halos, δb, and the square of the quadratic sum of the Miller indices for the basical paracrystalline plane, h^2. In the case of As_2Se_3, as well known, the basical layer plane in crystal is of type (001). The linear dependency $\delta b \sim f(h^2)$ could be an argument in favour of the existence of nano-paracrystals as constitutive elements of the As_2Se_3 glass.

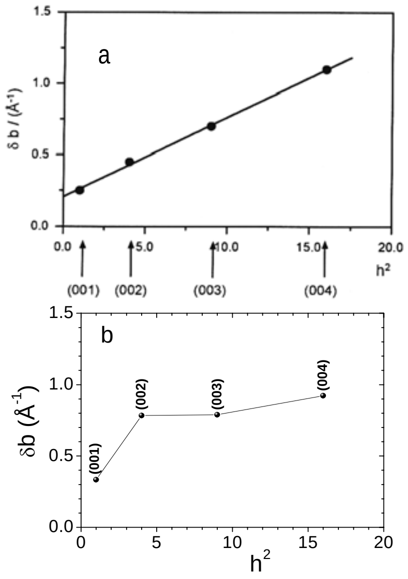

Fig. 1 a. The Hosemann plot for the nano-paracrystalline structure in As_2Se_3 glass. b. The Hosemann plot for the microparacrystalline structure in As_2S_3 glass.

From the Hosemann graph one can get two important parameters. The intercept of the line with the ordinate gives the value of 1/D, where D is the mean true nano-paracrystal thickness normal to the paracrystalline basical plane. From the slope of the line we can get the paracrystalline distortion parameter, *g*, as defined in the theory as the paracrystalline distance fluctuation, $g^2 = \left(\overline{d^2}/\overline{d}^2 - 1\right)^{1/2}$, where *d* is the net plane spacing and the other notations are the usual ones: $\overline{d^2}$ is the mean of d^2 and $\overline{d}$ is the average value of *d*. The mean true paracrystal thickness obtained for the As_2Se_3 glass, which is in fact the thickness of the layer packing in the glass structure, is 29.8 Å. This value is in agreement with the data estimated in the literature. Leadbetter and Apling [82] have estimated from the first peak a packing thickness of 20 - 22 Å, i.e. an average of four correlated layers. De Neufville et al. [83] reported a correlation length of ~ 40 Å in fresh, thin amorphous films of As_2S_3 and As_2Se_3. The paracrystalline distortion parameter, *g*, determined from the Hosemann's graph is 0.16. This means that the nano-paracrystallites in As_2Se_3 show strong deviations from the ideal crystalline structures ($g = 0$), but are also well under the limit of the complete disappearance of any crystal-like structural feature ($g = 1$). The Hoseman plot for As_2S_3 glass (Fig. 1b) is, nevertheless, quite different. The linearity is lacking. This behaviour can be interpreted as strong deviation of As_2S_3 from the crystalline deformed structure. What is in the depth is still a matter of controversy. We suggest that a strong tendency is manifested toward transformation from a disordered layer packing in a packing of closed clusters with double layer geometry.

The well expressed crystalline-like structural features in many glasses can be understood if one observes that during the amorphization process performed by applying high pressures, shock waves or by heavy particle irradiation, firstly disappear the crystallographic planes that are characterized by weak occupancy (low density). Finally it remains only the backbone of the structural order, the best connected structural planes. In the case of quartz (α - SiO_2) the experiments have shown that the amorphous state can be reached by applying high pressure. Before amorphization, under hydrostatic as well as non-hydrostatic stresses the material exhibits characteristic lamellar features [84]. The density of these lamellar configurations increases with the pressure. Fine planar deformation features occur on crystal planes and their dominant orientation is related to the peak stress. Below 12 GPa the dominant orientation is (0001). At higher pressures firstly (1013) and then (1012) orientations prevail. It is suggested that the amorphization results from the instability in the shear modulus in the (101n) planes.

In the case of chalcogenides, which are characterized by atomic coordination between 2 and 3, the basic layers in crystals lose the intrinsic order by amorphization but preserve the layer staking along the distances of the order of paracrystal thickness parameter. The type of structural element preserved in the glassy state seems to depend on the chemical composition of the material. Thus, there was firmly established that the dominant contribution to the FSDP in $GeSe_2$ glass is given by the Ge-Ge correlations [85]. This means that, primarily, the structural units based on tetrahedral germanium bonds are involved in the structural configuration responsible for the medium range order (MRO) and this fact is related to the better bonding and higher stability of the denser crystallographic planes based on packed germanium tetrahedra. The most stable structural planes of the corresponding crystalline phases re retained in the disordered materials with ill-defined packing and they give rise to MRO structural effects. The existence of long-lived crystal-like clusters in melt, before quenching, leads to a lower free energy for gas-like + crystal-like configuration than for homogenous gas-like atomic configuration [86]. Some investigators [87] presented facts that confirm the existence of long-lived crystal-like clusters in the liquid. Therefore the origin of crystal-like features in glass is easy to understand. The micro-paracrystalline theory, which is well defined for the lamellar and fibrous structures, seems to find in the chalcogenide glasses an appropriate working case.

Many specific phenomena, recently observed in chalcogenide glasses as p.g. photo-crystallization, photo-amorphization and photo-anisotropy [88] can be explained in the frame of the micro-paracrystalline model. The bond excitation in poorly formed paracrystallites can shift the thermodynamic equilibrium of the structural units (pseudo-layers) towards a better packing with long distance correlations or to a larger packing disorder, while polarized light can induce a preferential orientations of the pseudo-layer packing.

Recently, Tanaka and Nakayama [89] have demonstrated that the photoconductive spectral gap in glass is located at the same energy position as the band gap in the crystalline counterpart. On this base they affirm that such an electronic similarity must reflect the structural similarity in amorphous and crystalline chalcogenides. This feature can find a support in the paracrystalline model for glassy chalcogenides.

In the frame of the nano-paracrystal theory it is possible to explain all the characteristics and the complex behaviour of the FSDP, while new parameters useful for glass characterization can be extracted. The high sensitivity of the FSDP to various physical parameters can be explained by the existence of the basic paracrystalline configuration characterized by large packing distances. Bradaczek [90] has shown that the position and the intensity of the X-ray diffraction peaks changes differently in every diffraction order as a function of the paracrystal parameters. The FSDP, which represent the first order diffraction peak in the paracrystalline model, is, therefore, very sensitive to the modifications of the paracrystalline configuration in glass.

Finally, we would like to remark that in molten alloys based on metal (Au) and a thetrahedral covalent element (germanium) have been observed characteristic features under the form of small FSDP or prepeak on the main diffraction peak [91]. In the case of liquid Au20%- Ge80% this peak has been interpreted as due to heteroatomic associates of composition Au_4Ge, e.g. regular tetrahedra of Ge-Au_4, characteristic to the crystalline compound Au_4Ge. It is evident that even in the liquid phase we are dealing with structural organization of the complex melt as a disordered matrix where micro-paracrystals of specific composition are embedded. The self-organization of the paracrystalline elements is governed by the long-range forces that exist even in the liquid state at not too large temperatures.

2.3 The closed cluster model

Recently, a new model for the binary arsenic chalcogenide glasses has been proposed [64]. In this model the structural configurations consists in closed clusters of different extension. 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^o and the bond angle on arsenic 98.7^o (an average value) as reported by Rubinstein and Taylor [92].

The structures of minimum free energy have been calculated by an iteration procedure based on Monte Carlo – Metropolis method [93] 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 $V1=A(r^2-r_o^2)^2$ with $A=2.4\times10^{-5}$ dyn/$Å^3$ and the bond bending potential centered on the sulfur equilibrium bond angle and on the arsenic mean equilibrium angle between bonds was taken as $V2=B(\alpha-\alpha_o)^2$ with $B=2.04\times10^{-4}$ dyn.Å/rad [94].

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 [64]. 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. 2 (a2, b2, c2, d2).

The model could be extended to other low dimensional materials in the amorphous state, as e.g. amorphous arsenic. Fig. 2 (a1, b1, c1, d1). shows the nano-pie structure for the first member of the series. The

As-type 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 $As_2S(Se)_3$.

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 [64]. 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 of 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 inter-cluster interaction [95].

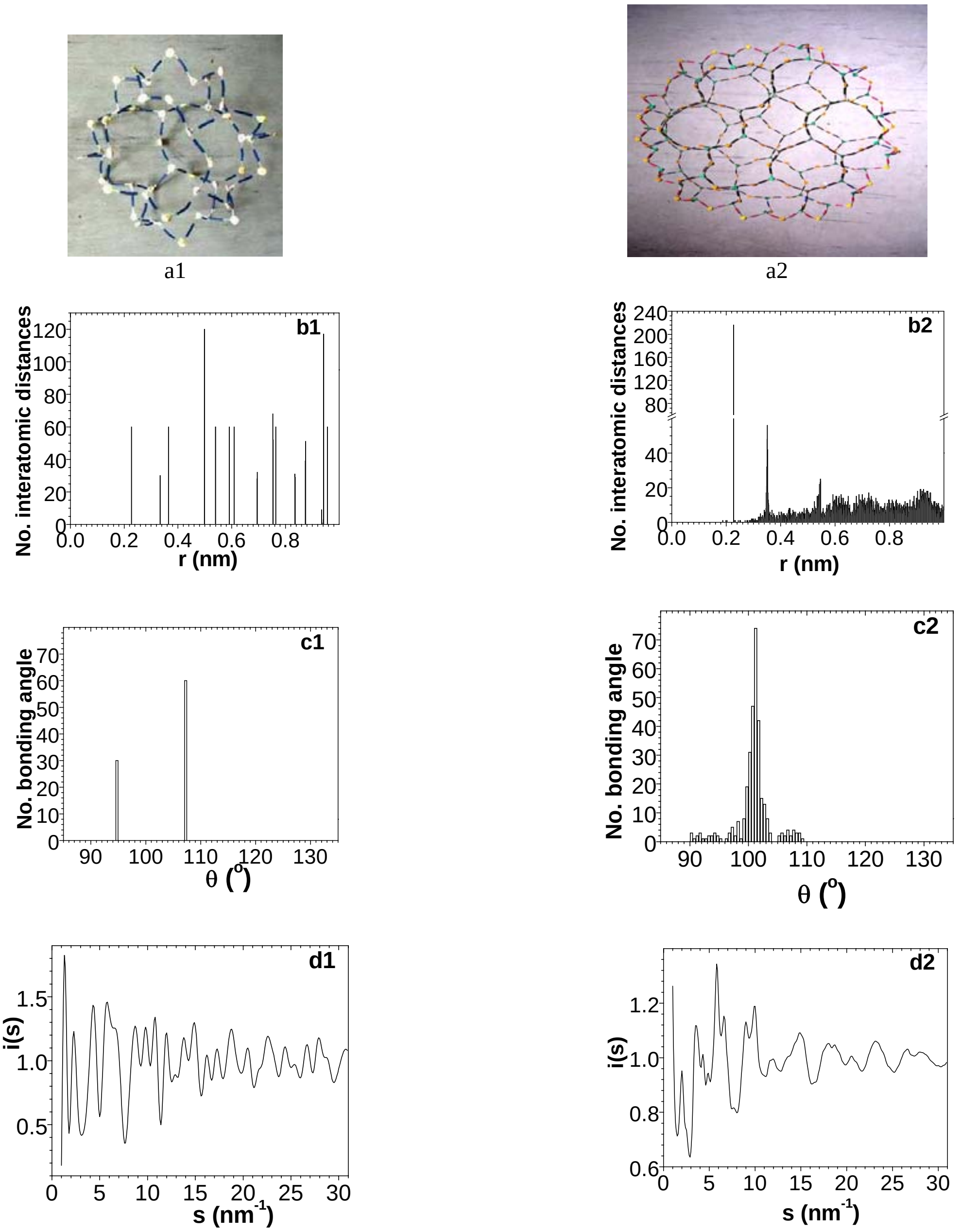

Fig. 2. 1 - The relaxed model of a big closed cluster of composition $As_{20}S_{30}$ (50 atoms); 2 – Relaxed nano-pie clusters of As_2S_3 ($As_{72}S_{108}$); a. the model; b. the structure factor; c. the pair distribution function; d. the bonding angle distribution (after relaxation).

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 photo-excited hole diffuse and are captured by the trap, then being trapped deeper through modifying the inter-cluster interaction. Lattice relaxation takes place. In this case, a photo-excited 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 photo-fluidity [96]. In the frame of the closed cluster model, the photo-fluidity 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 [97]. 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.

The ideal 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.

3. A possible general model for chalcogenide glasses

After analyzing various kind of models developed along more than 40 years of research in amorphous chalcogenides a new attractive model emerges.

The waved layers model is the simplest explanation of the structure of binary arsenic glass. The model succeed to explain the decrease of density during the phase transition from crystal to glass, and to account for the increase of the quasi-distance during phase transition crystal→glass. Nevertheless, the isotropy of the glass, as well as the low density of the dangling bonds cannot be explained by the model. On the other hand the paracrystalline model seemed to be attractive due to simple explanation of the glass as a slightly deformed crystalline lattice, thus accounting for the loss of the long range order. An important objection to this model is its structural stability. If the topology of the model remains the same as that of the crystal, why the lattice suffers deformations ? And, in fact, while the structure does not come back spontaneously to the initial structure (not deformed) ?. The paracrystalline model is not structurally stable and returns to crystal because, thus, the free energy can be lowered substantially.

The ideal closed cluster model seems to be more appealing for the explanation of the structure of the chalcogenide glass. The formation of more or less extended cluster with two layers that are linked to the margins, without allowing for dangling bonds, is possible from the crystallo-chemical point of view. For perfect closed clusters the valence alternation pairs (VAP), simply, does not exist. Nevertheless, experimentally, the presence of VAP's is demonstrated (low amount). Thus, we are forced to admit that the true model could be considered as a heap of closed and non-closed cluster, even with some addition of simple structural units, as short polymeric chains, small molecules or even short layers.

In conclusion, the model for a binary arsenic glass can be imaged as a random mixture of small, medium and large closed clusters, that are occasionally interpenetrated by open clusters and other polymeric units that interact with the main clusters and forms a rigid three-dimensional network without anisotropy.

The light induced effects consist in the structural changes at the interface between clusters, with the formation of large polymeric units or larger clusters in the glass network. This intermediary model eliminates the overall difficulty of the models that suppose the layers are extended indefinitely in the bulk glass, with many dangling bonds at the margins of the disordered layer.

The anisotropic phenomena induced by light could be also explained simply in the frame of the intermediary model. The polarized light can induce directional changes and even chiral long units, by polymerizing the double-layer clusters.

4. Conclusions

The structure of the amorphous binary glasses in the system As-Ch have been explained in terms of waved layers similars to those from crystal, in terms of slight deformations of the crystalline lattice (paracrystalline model) and as packing of large bi-layer clusters.

The best model seems to be an intermediate model. This model takes into account the existence in the structure of both open and closed mostly bilayer clusters with some admixture of other structural units as e.g. short layers, small molecules or even short or long polymeric chains.

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