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MICROPARACRYSTALLINE MODEL FOR MEDIUM RANGE ORDER IN COVALENT GLASSES

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The medium-range order in covalent glasses was analyzed in the frame of the paracrystalline theory. This theory, earlier applied to lamellar and fibrous structures, finds in the chalcogenide glasses an interesting working case.

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1. Introduction

There is continuous interest in the medium range order (MRO) or intermediate range order (IRO) of covalent glasses and metal-metalloid disordered materials [1]. MRO can be regarded as given by structural correlations in the range of 5-10 Å, in excess of those expected for an ideal Zachariasen-type continuous random network (CRN) characterized by a random dihedral-angle distribution [2].

The most remarkable manifestation of MRO in covalently bonded glasses is the so-called "first sharp diffraction peak" (FSDP) or "prepeak" in the structure factor S(Q). The characteristics of this peak (intensity, width and position on the scattering vector (Q) scale) are very sensitive to various physical parameters: temperature, pressure, irradiation... There was shown for several materials that the variation of the FSDP intensity with the temperature and with the aggregation state (solid-melt transition) is anomalous [3] in the sense that this peak increases reversibly with the temperature and becomes higher in the liquid state as opposite to the other peaks in the X-ray diffraction curve whose behaviour is normal (they decrease and become broader due to Debye-Waller factor).

2. Model for medium range order

Many attempts to interpret the experimental observations in various covalent glasses [4-6] have led to several models for MRO.

The first model supported by detailed calculations was the model with molecular clusters [7]. In this model the packing of As_4S_6 or As_4Se_6 molecules in arsenic chalcogenide thin films succeeded to reproduce the FSDP although with some arbitrariness in the choosing of the packing parameters.

More recently, Elliott [8] proposed a new model (void-based model or void correlation model) for the explanation of the FSDP in covalent glasses. According to Elliott's model, FSDP is a chemical-order prepeak due to interstitial volume around cation-centered structural units. The calculated positions of the FSDP for some covalent glasses (SiO_2, GeO_2, $ZnCl_2$, GeS_2, $GeSe_2$) agree well with the experiment and the anomalous temperature and pressure dependences of the FSDP can be thus explained in terms of density effects.

In the last years a renewed attention was paid to the old suggestion made by Vaipolin et al. [9] regarding the structure of the arsenic based chalcogenide glasses. Vaipolin supposed that the structure of these glasses consists in waved, disordered layers, similars to those known to exist in crystals. As

an example, the crystalline As_2Se_3 exhibits a layered structure [10] (Fig. 1) with each layer consisting of linked twelve-membered rings of alternated As and Se atoms.

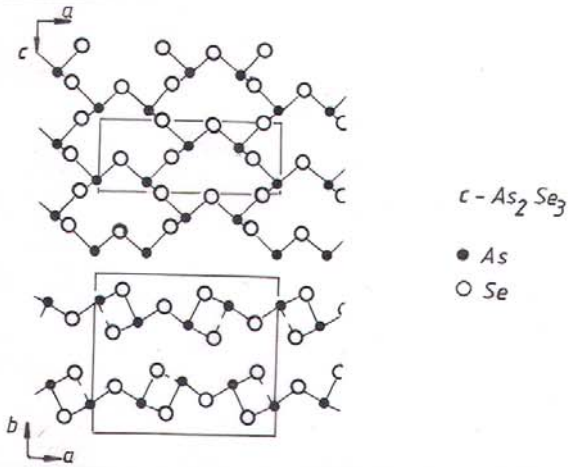

Fig. 1. The crystalline structure of an As_2Se_3 layer. The packing of the layers along the b axis is also shown.

The forces between adjacent layers are very weak compared to those within each layer [11]. There is a Bragg diffraction peak situated at Q = 1.26 $Å^{-1}$ known to correspond to the interlayer correlation. The glassy structure is characterized by several diffuse peaks in the structure factor S(Q). The first four peaks are shown in Fig. 2 (after Busse and Nagel [12]). Busse and Nagel [12] have shown that their experimental data are consistent with the existence of local layers in the As_2Se_3 glass. The structural picture suggested was of crimped, disordered As_2Se_3 layers. Estimates for the first peak width [13] have indicated that an average four layers are correlated.

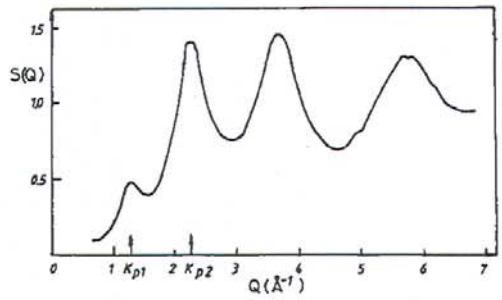

Fig. 2. The X-ray structure factor for glassy As_2Se_3. The first peak is FSDP and is located at Q1 = 1.27 ± 0.004 $Å^{-1}$.

On the other hand Fuoss and Fischer-Colbrie [14] claimed no evidence of layers in the $GeSe_2$ films as thin as 250 Å because the grazing incidence X-ray scattering pattern did not change with thickness and they concluded that, if there are layers, they have features which are different from the crystal and are not correlated in the same way.

Very recently Gaskell and Wallis [15] evidenced a correspondence between FSDPs in glasses and crystals and examined the anisotropic scattering from atomic models of glassy SiO_2. They proposed that quasilattice planes in glasses (as distinct from two dimensional layers), analogous to Bragg planes in compositionally equivalent crystals, reveal the origin of the FSDP in silica and, by extension, in other covalent glasses.

In general, the models for MRO fail, to a more or less extent, to reproduce all the particular features and the behaviour of the structure factors in covalent glasses.

The molecular cluster model fails in explaining the increase of the FSDP with temperature. If molecular clusters were present, the increase of the first peak would indicate that more clusters were forming or that they were becoming spatially better correlated as the temperature rises. The formation of clusters seems unlikely because it must be reversible (the FSDP changes reversibly with temperature). The thermal energy provided to the clusters would presumably prevent their increased correlation.

The void correlation model explains the FSDP increase with the pressure in the following way: application of the pressure causes a densification of the glass structure i.e. a diminishing of the interstitial volume and thus, it is expected that FSDP decrease correspondingly, as experimentally observed in SiO_2 glass [16] and As_2S_3 glass [17]. The anomalous temperature dependency of the intensity of the FSDP is predicated by the void correlation model since the FSDP intensity is expected to scale with the amount of void volume clustered around cation-centered units in the glass structure and the glass density decreases with the temperature. Nevertheless, the difference in the behaviour of the FSDP when the glass is subjected to uniaxial compression and when hydrostatic compression is applied cannot be explained satisactorily. FSDP maintains its position during uniaxial compression but shifts towards higher diffraction angles during hydrostatic compression. In both cases the peak intensity decreases [17].

In general, all the models for the structure of glasses take into account only the FSDP or the FSDP + the main diffraction peak and neglect the other details in S(Q). An overview of the full diffraction pattern reveals some surprising features and allows for suggesting a new more realistic model for MRO in large classes of covalent glasses.

3. Microparacrystaline model for medium-range order

We affirm that the experimental data on covalent glasses can be consistently explained in the frame of the paracrystalline theory developed by Hosemann [18].

Firstly, we would like to observe that in many chalcogenide glasses the halo peaks are located at the positions where intense diffraction peaks exist in the crystalline homologues. Fig. 3 shows, after Itoh [19], as examples, the case of As_2Se_3 and of three arsenic selenide glasses modified by Ag and by Cu. It is noteworthy that neither the glassy nor the crystalline Ag(Cu)-As-Se materials possess diffraction peaks at $2\theta = 17^\circ$, the FSDP position in glassy As_2Se_3. Therefore, the glasses show short range order (SRO) and medium range order similar to those of the crystalline counterpart compounds.

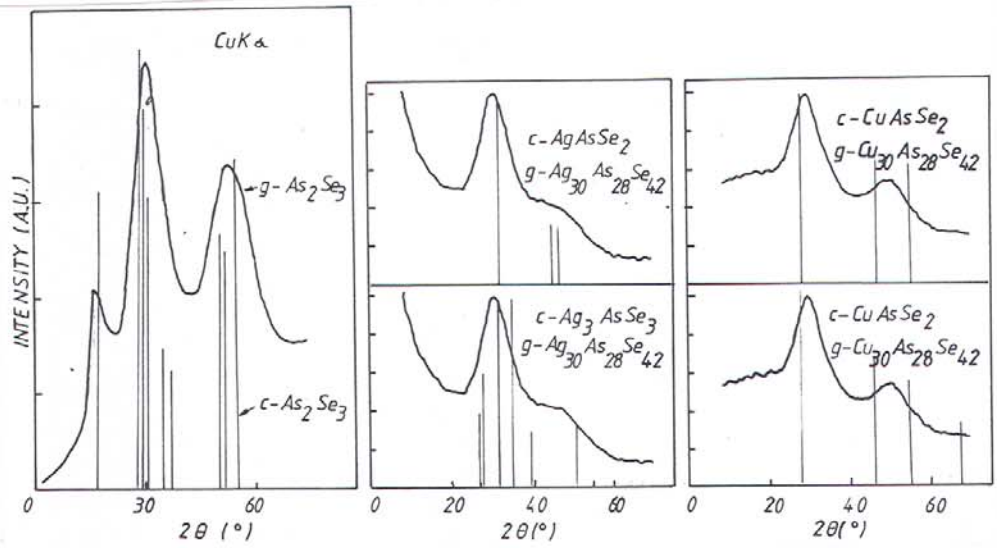

Fig. 3. X-ray diffraction of glassy (g) and crystalline (c) Ag(Cu)-As-Se glasses. Only intense peaks are shown in each crystalline diffraction pattern (After [19]).

Now, we look at the structure factor of the As_2Se_3 glasses from the point of view of the paracrystalline theory. The diffraction pattern of As_2Se_3 glass shows peaks at the Q positions, which roughly correspond to the first and higher diffraction order of 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 [20]. Indeed, as Fig. 4 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 layered compunds, the basical layer plane can be assimilated to a (001) plane. The linear dependence $\delta b \sim f(h^2)$ is a strong argument in favour of the existence of microparacrystals as constitutive elements of the As_2Se_3 glass.

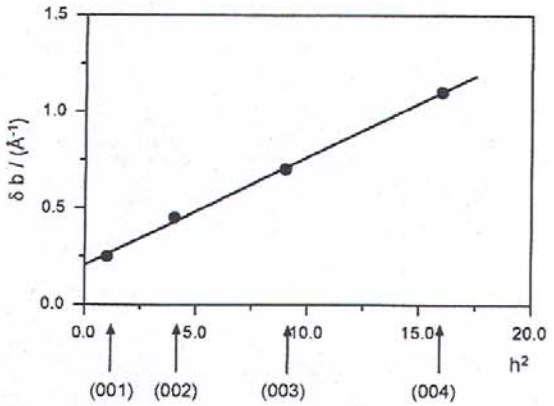

Fig. 4. The Hosemann plot for the microparacrystalline structure in As_2Se_3 glass.

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 microparacrystal 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 relative paracrystalline distance fluctuation, $g^2 = \left(\overline{d^2} / \bar{d}^2 - 1\right)^{1/2}$, 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 $\bar{d}$ 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 [21] have estimated from the first sharp diffraction peak a packing thickness of 20 ÷ 22 Å, i.e. an average of four correlated layers. De Neufville et al. [22] 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 microparacrystallites 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 ($g = 1$).

4. Discussion

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 vanish the crystallographical 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 pressures. Before amorphization, under hydrostatic as well as non-hydrostatic stresses the material exhibits characteristic lamellar features [23]. 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 (101 n) planes.

In the case of chalcogenides, which are characterized by mean atomic coordination between 2 and 3, the basical layers in crystals loses the intrinsic order by amorphization but preserves the layer stacking 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 [24]. This means that, primarily, the structural units based on tetrahedral germanium bonds are involved in the structural configuration responsible for the 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 subsist 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 homogeneous gas-like atomic configuration [25]. Some investigators [26] presented facts confirming 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 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 e.g. photo-crystallization, photo-amorphization and photo-anizotropy [27] can be explained in the frame of the microparacrystalline 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 orientation of the pseudo-layer packing.

Recently, Tanaka and Nakayama [28] have demonstrated that the photoconductive spectral gap is located at the same energy position as the band gap in the crystalline counterparts. 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 strong support in the microparacrystalline model for the non - crystalline chalcogenides.

In the frame of the microparacrystalline theory it is possible to explain all the characteristics and the complex behaviour of the FSDP, while new parameters useful for glas characterization can be extracted. The high sensitivity of the FSDP to various physical parameters can be explained by the existence of the basical paracrystalline configuration characterized by large packing distances. Bradaczek [27] 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 [28]. In the case of liquid Au - 20% Ge 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 our opinion that even in the liquid phase we are dealing with structural organization of the complex melt as a disordered matrix where microparacrystals 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.

5. Conclusions

A new model for medium-range order in non-crystalline solids was advanced, based on the paracrystalline theory of disordered solids. The microparacrystalline model applied to chalcogenide glasses seems to be of interest both for the description of MRO in such glasses and for understanding of their crystallization and melting.

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