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Letter to the Editor

THE MEDIUM-RANGE ORDER AND THE INTERFERENCE FUNCTIONS OF STRUCTURAL MODELS OF $Ge_{20}As_{40}Se_{40}$ AND $Ge_{30}As_{20}Se_{50}$ AMORPHOUS ALLOYS

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The clearest evidence of the existence of a certain medium-range order in Ge and As chalcogenide glasses [1,2] is the appearance of a first sharp diffraction peak (FSDP) in the diffraction spectra around $s = 1$ Å^{-1} (s being the scattering vector modulus) associated with correlation lengths around 15–20 Å. The study of this peak could be glossed over in a local order analysis but its elucidation is of interest in a tridimensional structural model. On the basis of how a theoretical diffraction experiment on a sample equal to the model reproduces the FSDP, we attempt to connect the spatial features of the models with the topological characteristics predicted in the literature [3].

It seems to stand to reason that if a model accounts for the information provided by the FSDP, it must somehow appear in the interference function which would correspond to the proposed model. This function was achieved as the Fourier transform of the model correlation function, $G_{\mathrm{mod}}(r)$:

$$s.i_{\mathrm{mod}}(s) = 4\pi \int_0^{R_{\max}} G_{\mathrm{mod}}(r) \sin sr \, \mathrm{d}r. \tag{1}$$

Since this function depends on the model size, an "experimental" interference function was obtained to compare the result as:

$$s.i'(s) = 4\pi \int_0^{R_{\max}} G(r) D(r) \sin sr \, \mathrm{d}r. \tag{2}$$

$D(r)$ being a dumping function which simulates the shape and size of the model [4].

The models (spherical and of 20 Å diameter) were generated by fitting their theoretical RDF to the experimental one for r values between 0 and 10 Å, above which there may exist incorrect correlation lengths. The integration of eqs. (1) and (2) was carried out till $R_{\max} = 10$ Å only, following the line undertaken in previous studies [5].

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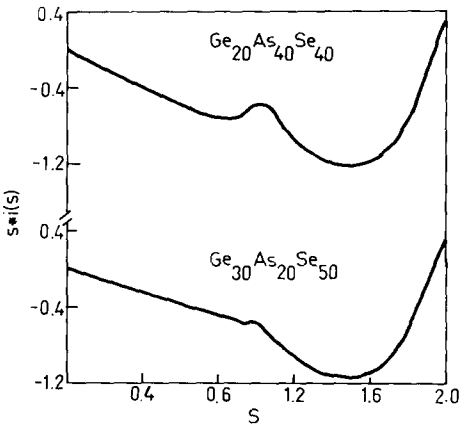

Fig. 1. Experimental interference functions of both alloys, showing the FSDP.

Plots of the experimental interference function in the s interval 0–2 $Å^{-1}$, showing the referred FSDP, appear in fig. 1. As regards the $Ge_{20}As_{40}Se_{40}$ alloy its model interference function (fig. 2a, dotted line) reproduces a flattened peak as does the "experimental" function (calculated according to eq. (2)). Although the model has been designed to describe correlation lengths below 10 Å, it can be deduced from this that, despite the model size, some medium-range traces are present. Since the Fourier transform of experimental $G(r)$ (fig. 2a, full line) achieved with $R_{max} = 10$ Å does not totally reproduce the FSDP, and its shape is similar to that corresponding to the model, we think that this flattening could be due to the reproduction of a certain medium-range order by the model but whose total description is hindered by the small size of the model.

Both models, consisting of a tetrahedral framework linked to each other by means of either another Ge atom or As and Se chains, some of these chains as independent structural units, were achieved in previous works [6,7] by means of a technique described in ref. [8] based on the Monte Carlo method. Figs. 3 and 4 are spatial representations of the models, the outstanding difference between them being a greater continuity in the model corresponding to the $Ge_{30}As_{20}Se_{50}$ alloy.

J.C. Phillips proposed, as the main feature of an approximately perfect covalent glass network, the agreement between the number of degrees of freedom per atom and the number of configurational constraints imposed by the valence force field interactions of bond-bending and bond-stretching. When the number of constraints exceeds the number of degrees of freedom, Phillips assumes that partial breakdown of the chemical order occurs. As a topological consequence of this "the network continuity will be interrupted and molecular clusters will be formed, may be cross-linked in a few places" [3]. These features seem to tally with the characteristics shown by the model (fig.

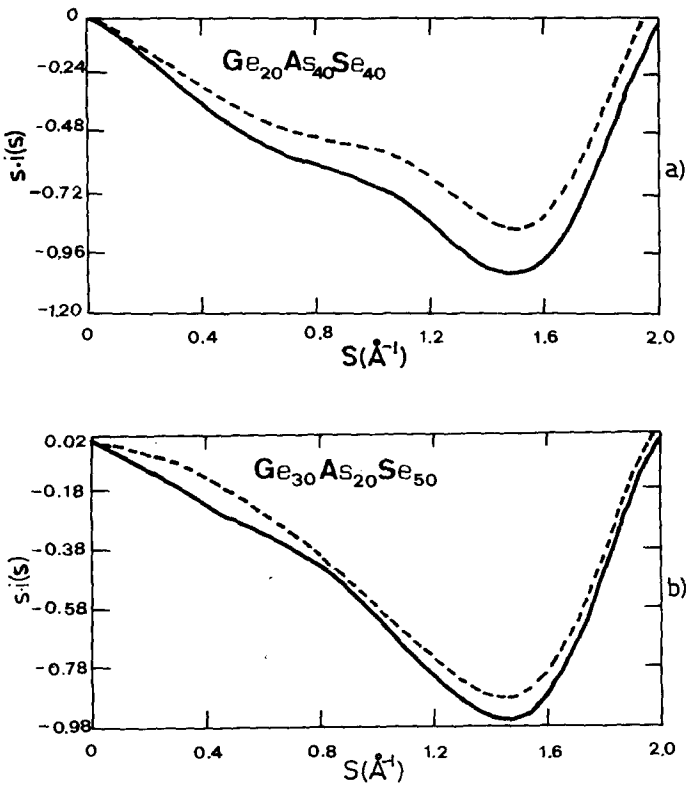

Fig. 2. a, b – $s.i'(s)$ and $s.\ i_{mod}(s)$, full line and dotted line, respectively, for both alloys.

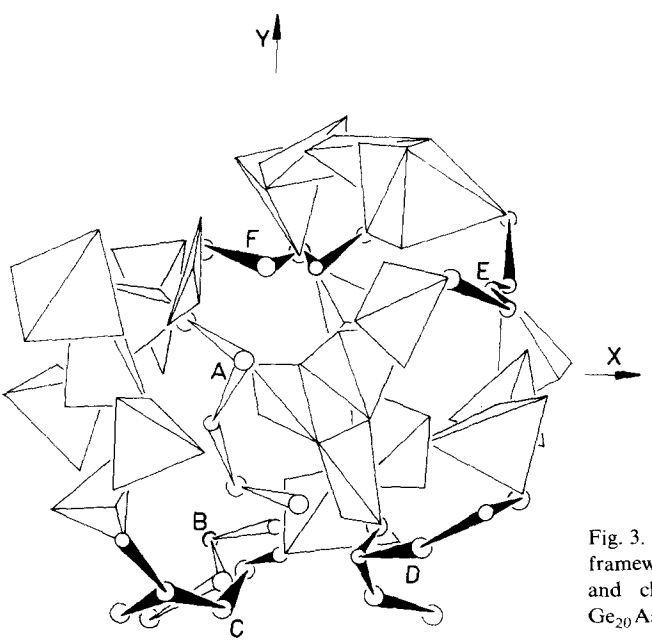

Fig. 3. Spatial representation of the framework of tetrahedra clusters and chains for the amorphous $Ge_{20}As_{40}Se_{40}$ alloy model.

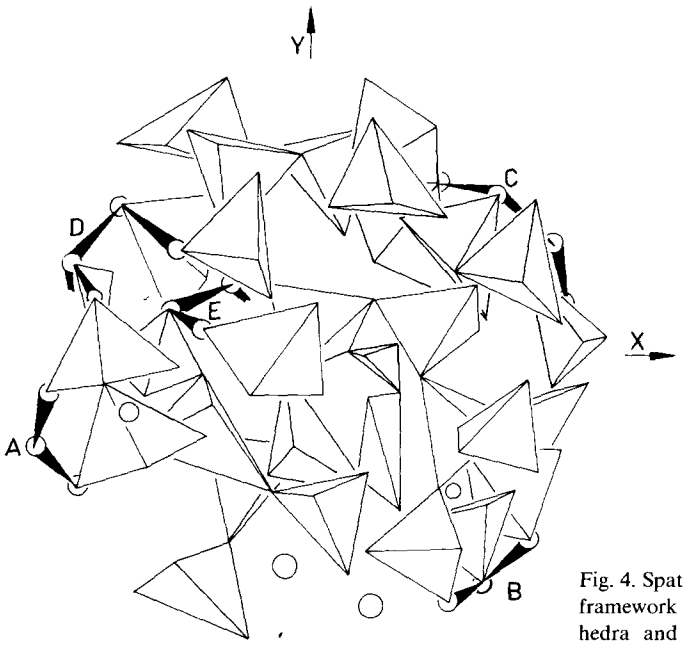

Fig. 4. Spatial representation of the framework of continuous tetrahedra and chains for the amorphous $Ge_{30}As_{20}Se_{50}$ alloy model.

4), so that we suggest tetrahedra clusters, containing around 30 atoms, as medium-range feature of this alloy.

Likewise, the experimental interference function of the $Ge_{30}As_{20}Se_{50}$ alloy presents the FSDP, but it is found at $s = 0.99$ Å^{-1} and less intense than that of the $Ge_{20}As_{40}Se_{40}$ alloy found at $s = 1.02$ Å^{-1}, both shown in fig. 1. From that it may be inferred that the former corresponds to greater molecular clusters with longer correlation lengths, apparently borne out by the Fourier transform of experimental $G(r)$ with $R_{max.} = 10$ Å, which barely accounts for it.

On the other hand, experimental results point out a greater compacity of this alloy since the weighted average number of first neighbours, calculated from the area beneath the RDF first maximum, is 2.97 at. [9] whereas the value found for the other alloy was 2.76 at..

Moreover, along the same lines but from a topological viewpoint, this alloy must be a little more constrained than $Ge_{20}As_{40}Se_{40}$ since the number of constraints per atom, defined in the sense of Lagragian mechanics as [10],

$$N_1 = \Sigma x_i \frac{m_i^2}{2},$$

m_i being the coordination of the i-atom, is 4.3 as opposed to 4.2 for the first alloy.

Looking at the Phillips proposition [10], in a covalent network, the greater the constraint, the greater the continuity, in such a way that the medium-range

order tends to the long-range order. Consequently, under this condition, rather larger clusters would be formed and, hence, longer correlation lengths will be involved, a may be expected from the respective FSDP position. It seems to stand to reason that small size effects must be more pronounced in order to describe the medium-range order as can be appreciated in fig. 4 where the tetrahedral network is more continuous than in the other model.

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