Computer-Generated Models of *a*-SiSe$_2$: Evidence for a Glass Exhibiting Medium-Range Order

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A new approach to modeling glass structures is presented, with specific application to *a*-SiSe$_2$ and the medium-range order exhibited by this system. A systematic investigation of the parameter space describing amorphous structures has been undertaken, and the effect of different structural features on the total pair correlation function studied. This work suggests that the structure of *a*-SiSe$_2$ consists of both randomly oriented chains of edge-sharing Si(Se$_{1/2}$)$_4$ tetrahedra and cross-linked chain-cluster units.

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A major unresolved problem in the field of glass science is the type and extent of medium-range order (MRO). The existing experimental structural probes give, at the best, only ambiguous information about MRO and, therefore, structural modeling studies are a potentially useful tool for such investigations. The philosophy behind this modeling approach is to construct completely computer-generated models of a glass structure, allowing full control over the geometry of the structural units (e.g., dihedral angle) and the development of the model (e.g., "flexibility" of random chains). Specific features constituting MRO within the system are included as "seeds," from which the random matrix of the structure may be generated. By our systematically varying the parameters describing both the model generation and the seeds themselves, the influence of each on the resulting total pair correlation function, $T(r)$ may be studied; over 500 models were built in the course of this study.

The glassy system chosen for study is expected to contain a high degree of MRO resulting from the specific type of connection of structural polyhedra in the glass. Both high- and low-pressure polymorphs of crystalline SiSe$_2$ are known to exist; the low-pressure polymorph is orthorhombic ($C42$ type) containing parallel chains of *edge*-sharing tetrahedra,[1] the basic repeating unit being Si$_2$(Se$_{1/2}$)$_8$, while the high-pressure polymorph[2] has a tetragonal structure containing SiSe$_4$ tetrahedra which share vertices to form a 3D network. Strong similarities have been reported between the Raman spectra of the glass and the *low*-pressure polymorph of *c*-SiSe$_2$, thereby suggesting that the basic structural unit in both is the same. Further Raman and infrared studies have shown that interpretation of such vibrational spectra requires the MRO in the glass to extend beyond the existence of chains of edge-sharing Si$_2$(Se$_{1/2}$)$_8$ units to include spatial correlations between such chains; "packets" of edge-sharing tetrahedral chains[3] and cross-linked chain clusters (CLCC's)[4] have been proposed to explain these vibrational data.

The primary aim of this study of *a*-SiSe$_2$ was to investigate the ability of structural models to discriminate between continuous-random-network (CRN) models, and models containing either only random chains of edge-sharing tetrahedra or "features" such as microcrystallites and CLCC's which are incorporated into a random-chain matrix. The total pair correlation function $T(r)$ $[=J(r)/r]$ was calculated for each model and

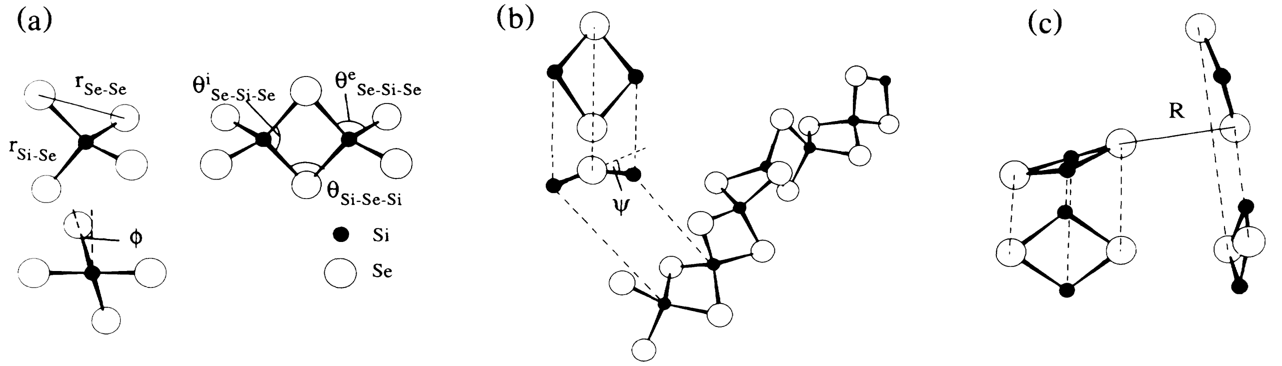

FIG. 1. (a) The geometry of the basic tetrahedral unit. The planes defined by the selenium pairs and the central silicon atom are perpendicular in an undistorted unit—the dihedral angle, ϕ, is defined as the relative rotation of the two planes from this perpendicular orientation. (b) A "random-chain" seed is shown, and the bending angle, ψ, is indicated. The relationship of the seed to the final random chain is also shown. (c) A "locally parallel" seed. The distance R is the interchain Se-Se separation.

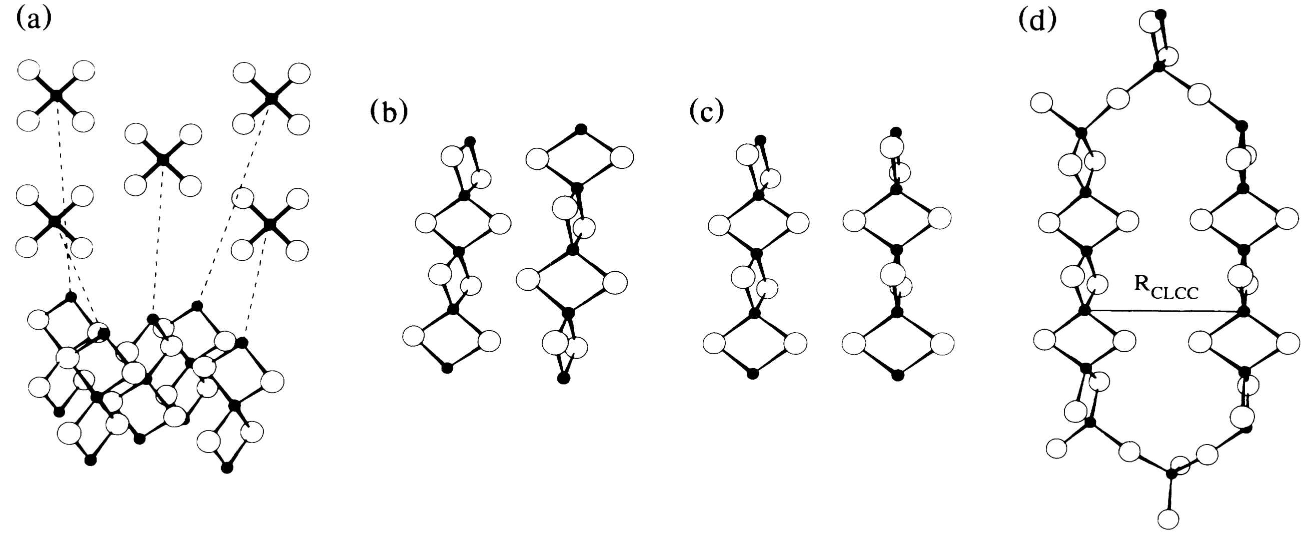

FIG. 2. (a) The crystal unit cell of the low-pressure polymorph of c-SiSe$_2$ (Ref. 1). The projection is shown in the upper part of the figure. (b) Two parallel chains exhibiting "antiphase" parallelism. (c) Two parallel chains exhibiting "in-phase" parallelism. (d) A cross-linked chain cluster (Ref. 4).

compared with that obtained from the neutron-scattering data of Johnson.[5] All models were built to a density of 0.0105 Si atoms Å^{-3}, in agreement with the density of 3.25 g cm^{-3} indicated by Johnson *et al.*[6]

The algorithm may be summarized as follows. The structures, containing about 1200 atoms, were generated from seeds which were placed at random, and in a random orientation, on a cubic grid. The seeds used are shown in Figs. 1 and 2.

Random-chain seeds.—These units are used as starting points for the chains. Their number will control, to some extent, the distribution of chain lengths within the final model—the more seeds there are, the shorter the average chain length. Two edge-sharing tetrahedral units [Fig. 1(a)] are placed back to back, but terminate on a Si atom each time as shown in Fig. 1(b). The angle denoting the deviation of successive tetrahedral units from the straight chain structure, ψ, is a random variable ($\psi \leq \psi_{\max}$) which allows the chains to "bend." A typical random chain is illustrated in Fig. 1(b). Both the bending angle, ψ, and the dihedral angle, ϕ, as well as the various bond angles and the bond length illustrated in Fig. 1, were systematically varied to investigate their effects on $T(r)$ in order to obtain the best agreement

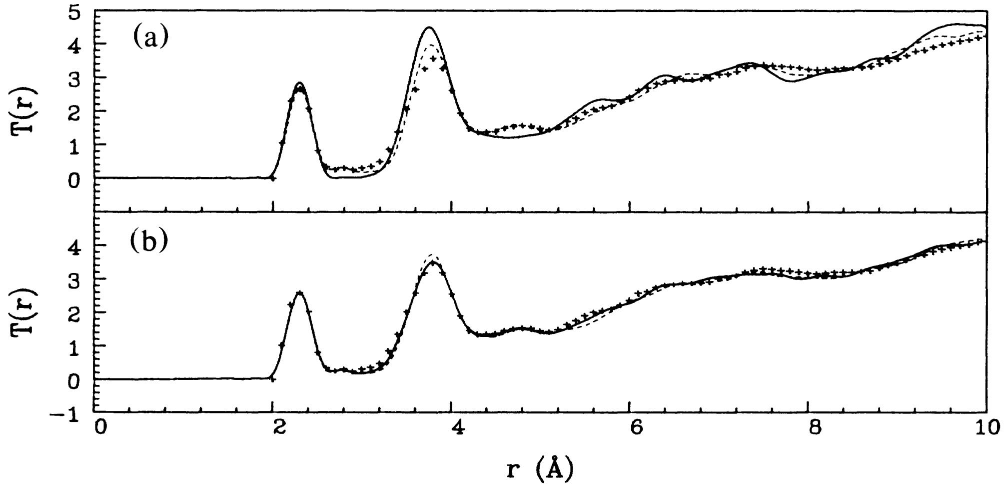

FIG. 3. (a) Comparison of $T(r)$ calculated for a pure CRN (solid line) (of bond length 2.3 Å and Si—Se—Si bond angle 90°) and for a pure random-chain model (dashed line) with the experimental data of Johnson (Ref. 3) (crosses). (b) The $T(r)$ calculated for a typical microcrystallite-based model (dashed line) and that of the model which gave the best correlation (solid line) with experimental data (crosses).

with experiment.

The following types of seeds have been considered so that their possible contribution to any MRO in the system may be studied.

Locally parallel seeds.—These seeds provide a minimal parallelism between selenium atoms on neighboring chains. The basic unit is shown in Fig. 1(c) and consists of two random-chain seeds which are positioned as a single unit with the selenium atoms in an orientation, similar to that found in the crystal (i.e., selenium pairs on adjacent chains are approximately perpendicular to one another—this configuration will be referred to as "antiphase" parallelism). The effect of this type of seed is to produce a noncrystalline unit which forces two chains to be locally parallel, as opposed to randomly oriented, with respect to one another; hence during the growth and relaxation phase of the modeling the chains are given a greater opportunity to align themselves if such an arrangement is structurally or energetically favorable.

Microcrystallite seeds.—The crystal unit cell is shown in Fig. 2(a). A microcrystallite of any dimension may be added. Two different sets of bond lengths and bond angles were used to describe these units and both were investigated: (a) regions which have the same bond angles and bond length as in the true (low-pressure) crystal structure[1]—i.e., *microcrystals*; and (b) regions of *crystallinity* which have a crystal-like structure, but possess bond angles and bond lengths characteristic of the random chains. With use of these microcrystallites, regions of pure *crystal* or of *crystallinity* may be introduced into the model. The separation between the chains is determined by our keeping the same interchain Se-Se distance and symmetry as in the crystal. This type of seed was also used to model regions of pairs of chains running parallel to one another, over lengths greater than two tetrahedral units [see Figs. 2(b) and 2(c)]. It is noted that the existence of adjacent chains "in phase" with each other [Fig. 2(c)] allows the chains to distort through small angles at the selenium "hinges" (where four seleniums, two from each chain, are parallel), thereby maintaining the parallelism and hence the interchain correlations, but reducing the well-defined intrachain correlations which can give rise to too much structure in $T(r)$ at $r \geq 6$ Å.

Cross-linked chain clusters.—A typical CLCC structure is shown in Fig. 2(d). These units consist of two parallel regions of chain which are cross linked as shown to form a closed loop. The cross links form chain ends from which further growth is possible, and the parallelism along the chain is of the form shown in Fig. 2(c), thereby allowing the units to distort through large angles, while remaining parallel. The final CLCC structure has three variables which may be altered: (a) the interchain separation, R_{CLCC}; (b) the number of tetrahedral units forming the parallel section of the CLCC—this must be odd to allow cross linking; and (c) the angle, ψ, by which the chains are allowed to distort at the hinges.

CRN models.—A CRN model was produced by our taking the coordinates of the Gaskell and Tarrant model[7] of a-SiO$_2$ (which contains only corner-sharing tetrahedra) and replacing the oxygen atoms with selenium atoms. The Si—Se—Si bond angle and Si—Se bond length were then varied, assuming the Se—Si—Se angle to be the pure tetrahedral angle.

Energy relaxation of all the models constructed was performed with the Keating[8] expression for the local strain energy, with an additional Lennard-Jones 12-6 potential approximating nonbonded interactions. The relaxation was achieved by the movement of all atoms simultaneously in the direction of the force acting on each, a distance proportional to that force.[9]

A complete discussion of the parameter space and conclusions drawn from this study will be given elsewhere; only the major results are presented below. Figure 3(a)

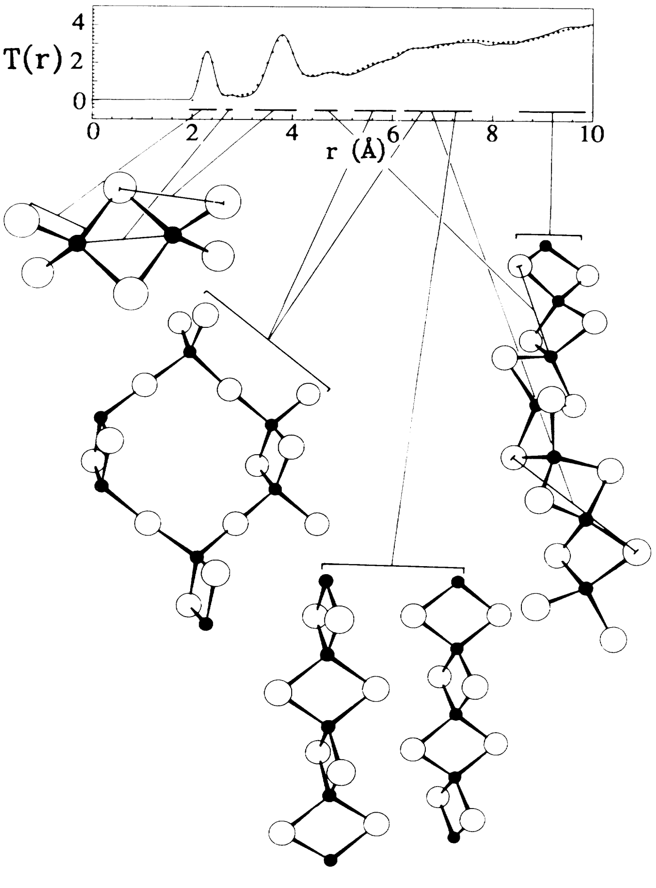

FIG. 4. The model showing the best correlation with neutron data contains ≃15% of its atoms in CLCC units and a further ≃15% in locally parallel seeds. The various structural features most strongly affecting $T(r)$ are indicated diagrammatically.

shows the $T(r)$ associated with models containing only CRN and only random-chain structures, respectively. Figure 3(b) shows the $T(r)$ corresponding to the model giving the best agreement to the $T(r)$ obtained from neutron diffraction. A typical $T(r)$ obtained from a microcrystalline model is also shown in Fig. 3(b), from which it is seen that microcrystalline regions embedded in a random-chain matrix produce good agreement with experiment in the 6–8-Å region. However, at microcrystallite concentrations greater than 15% too much structure is produced in the 8–10-Å region and, further, it is impossible to model both the second-peak shape and the 5–8-Å region simultaneously with use of any microcrystallite-based model. The limit placed on the microcrystallite content in the glass was found to be relatively insensitive to any density decrease following energy relaxation. A CRN description of a-SiSe$_2$ is also found to be inappropriate. In the range of Si—Se—Si bond angles investigated (60°–120°) the feature occurring at ~2.8 Å and the third peak in the experimental $T(r)$ are both missing or, at best, very ill defined. These features are strongly evident in the $T(r)$ obtained from the random-chain models [Fig. 3(a)], thereby providing strong support for a random-chain–based model of a-SiSe$_2$. Even the random-chain model provides poor agreement with $T(r)$ in the 5–6-Å region, and it is found that regions of parallel-running chains in phase with each other provide the required correlations. The second peak, however, still remains too narrow. The introduction of *corner-sharing* tetrahedra to join two in-phase parallel chains (thereby forming the CLCC unit proposed by Griffiths *et al.*[4]) broadens the second peak and also provides a way in which two chains may be held in a parallel configuration. The model giving the best fit to the experimental data contains both CLCC and locally parallel seeds with approximately 15% of the atoms in the total model being involved in each type of seed; the remainder of the model is formed from edge-sharing tetrahedral chains of mean length seven units. The $T(r)$ calculated for this model is shown in Fig. 3(b) and also in Fig. 4 where each structural feature and its associated contribution to $T(r)$ is indicated. CLCC's containing three or more tetrahedral units along the parallel region were found to give too much structure at high r in $T(r)$.

In summary, a systematic investigation of parameters characterizing the a-SiSe$_2$ structure has enabled the elimination of possible structural features in the glass. In particular, CRN and microcrystallite-based models are shown to be inappropriate for the a-SiSe$_2$ system. The edge-sharing tetrahedral arrangement characteristic of a-SiSe$_2$ is particularly favorable for the production of MRO (in the form of parallel chains). This modeling approach may readily be extended to the study of structure and MRO in other glass systems, e.g., organic polymeric systems and inorganic covalent glasses.

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