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CONF-880623--4

DE89 004267

October 1988

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Distribution:

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Presented at 11th International Symposium on the Reactivity of Solids,
Princeton, University, Princeton, NJ, June 19-24, 1988.

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*Work supported by the U.S. Department of Energy, BES-Materials Sciences,
under Contract #W-31-109-ENG-38.

A MOLECULAR DYNAMICS STUDY OF SiSe_2 GLASS ^{\$}

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Abstract

We report the results of a molecular dynamics study of molten and glassy SiSe_2 using an effective interparticle interaction. Results for the partial pair-correlation functions, partial structure factors, bond-angle distributions and statistics of rings are reported. Results are in good agreement with the neutron diffraction experiments.

Keywords: Molecular Dynamics Simulation
Chalcogenide Glass
Structure
Compound Keyword: Silicon diselenide.

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^{\$}Work supported by U. S. Department of Energy, BES- Materials Sciences, under Contract #W-31-109-ENG-38

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1. INTRODUCTION

A great amount of effort has been made in the last few years to obtain a better understanding of the chalcogenide glasses, particularly those involving Si and Ge as companions. For the SiSe_2 glass, neutron diffraction and Se K-edge extended X-ray absorption fine structure (EXAFS) [1] have determined that the coordination numbers for Si and Se are 4 and 2, respectively. The vibrational properties of SiSe_2 glasses have been studied by Raman scattering [2-4] and inelastic neutron scattering [5] confirming the existence of local units made of tetrahedra. An extensive comparison between the crystalline and glassy spectra was performed by Griffiths et al. [6].

A lot of attention has been paid to the nature of the first sharp diffraction peak (FSDP) that appears to be a common characteristic of a large number of chalcogenide glasses [7]. The FSDP reflects the intermediate range order since it is related with correlations beyond the nearest neighbor distances in the system.

The purpose of this paper is to report the structural results of a molecular dynamics (MD) simulation for the SiSe_2 system using a realistic interaction potential. In Section 2 we give the functional form of the potential and summarize the calculation; The structural correlations for the system and the connectivity of the local units of the glass are given in Section 3. Section 4 is devoted to the discussion, including the possibilities of improvement of the present model.

2. MD CALCULATION

In order to simulate the SiSe_2 system we have developed an interaction potential, which accounts for the Coulomb interaction between the ions, a charge-dipole interaction arising from the large polarizability

of Se ions and the steric repulsion due to the size of the atoms. Its functional form is given by

$$\Phi_{ij}(r) = \frac{Z_i Z_j}{r} - \frac{\frac{1}{2} (\alpha_i Z_j^2 + \alpha_j Z_i^2)}{r^4} e^{-r/r_{4s}} + A_{ij} \left(\frac{\sigma_i + \sigma_j}{r} \right)^{\eta_{ij}} \quad (1)$$

where Z_i , α_i and σ_i are the effective charge, the electronic polarizability and the size of the i th ion. The exponential screening term in the charge-dipole interaction is included in order to cutoff the range of the r^{-4} term at a reasonable distance. As usual, the Coulomb interaction is treated by the Ewald method which avoid problems with the low convergence of the $1/r$ term for large distances.

The simulation in the glassy phase was performed for a system of 648 particles (216 Si and 432 Se) in a cubic box of size 27.380 Å which gives the correct experimental number density $\rho=0.0316$ particles/Å³ at room temperature [8]. For the molten phase, a box of 28.102 Å gives the number density 0.0292 particles/Å³. In Eq. (1), the parameters Z , α , r_{4s} and σ_{Se} were taken to be the same as for GeSe₂. σ_{Si} was chosen to be smaller than σ_{Ge} and the repulsive constant A was determined by demanding that the pressure in the molten phase of SiSe₂ should be slightly positive. The effective interactions are plotted in Fig. 1.

A time step $\Delta t=3.0 \times 10^{-15}$ sec was used to integrate the equations of motion through the Beeman's algorithm [9]. The glass was obtained by quenching from the melt during an MD run of 20000 Δt in which a small amount of kinetic energy was removed at each 50th Δt . The system at a given temperature was thermalized for additional 6000 Δt

followed by the calculation of averages on another 6000 Δt .

3. STRUCTURAL RESULTS

In order to obtain the bond lengths for the system we calculated the partial pair-distribution functions, $g_{\alpha\beta}(r)$, shown in Fig. 2. We see that Si-Se has a very sharp peak at 2.25 Å, Si-Si has a small peak at 3.2 Å while the highest one is at 4.2 Å and Se-Se has its first peak at 3.75 Å. The dotted lines in the figure show the coordination numbers obtained by integrating the corresponding $g_{\alpha\beta}(r)$; there is a very clear shell of coordination four in the Si-Se distribution, which indicates that the structure is made of tetrahedra. In order to clarify this issue, we calculated the bond-angle distribution functions (Fig. 3), by choosing 4.6, 3.0 and 5.2 Å as the cutoff distances for Si-Si, Si-Se and Se-Se, respectively. Here for "bond" we mean a pair of particles within the given cutoff. The sharp distribution of Se-Si-Se angles around 108° together with the first peaks of Se-Se-Si at 36° and Se-Se-Se at 59° when compared with the angles in a perfect tetrahedron (109.5°, 35.25°, and 60°) give rise to the scenario where we have a network of slightly distorted tetrahedra.

The question about the connectivity between the tetrahedra can be addressed by examining the bond-angle distributions involving two or three Si. The peak at 60° for Si-Si-Si is a clear evidence that we have 3-fold rings, i. e., a closed path formed by three corner-sharing tetrahedra. In fact from the Si-Se-Si distribution one can see that the proportion of corner-shared tetrahedra (120°) is much larger than that for edge-shared (90°).

Figure 5 shows the neutron static structure factor, $S_n(q)$, of

vitreous SiSe_2 , which is calculated from the partial static structure factors, $S_{\alpha\beta}(q)$, according to the formula

$$S_n(q) = \frac{\sum_{\alpha\beta} b_\alpha b_\beta (c_\alpha c_\beta)^{1/2} \{ S_{\alpha\beta}(q) - \delta_{\alpha\beta} + (c_\alpha c_\beta)^{1/2} \}}{\left(\sum_{\alpha} c_\alpha b_\alpha \right)^2} \quad (2)$$

where the b 's are the neutron scattering lengths, the c 's are the concentration of each specie and $S_{\alpha\beta}(q)$ is given by

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4 \pi (\rho_\alpha \rho_\beta)^{1/2} \int_0^\infty r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin(qr)}{qr} dr \quad (3)$$

where the ρ 's are the number density of each specie. The overall agreement in height and shape between simulation and experiment is quite good except that the position of the first sharp diffraction peak (FSDP) is at $1.35 \text{ \AA}^{-1}$ instead of $1.0 \text{ \AA}^{-1}$, which is the experimental position. This discrepancy appears to be inherent in the model potential itself, since the same disagreement was found in a simulation of glassy GeSe_2 by Vashishta et al. [10] and later confirmed in a hypernetted chain (HNC) calculation by Iyetomi et al. [11]. It is well known that the FSDP arises from correlations of intermediate range order (beyond $4 \text{ \AA}$) which involves the connectivity of several tetrahedra. The MD simulation provide us with more detailed structural information, better than any experimental technique, since we know the positions of the particles at each time step. From the calculated partial static structure factors, shown in Fig. 5, one

can obtain some information on the contributors for the FSDP: neglecting the neutron scattering lengths, we see that the main part comes from the Si-Se and Si-Si correlations, and in much less extent from the Se-Se contribution.

The statistics of rings, defined as the shortest closed path made of Si-Se bonds for a given Si in the system, gives an alternative way of analyzing the structure. As the distances involved in these rings range from the nearest neighbor distance to several neighbors away, statistics in the short and intermediate range distances is achieved. The distribution of rings from size 2 up to ring size 9 for twenty configurations of the glass were calculated and the absolute number of rings and the number of rings per Si are given in Table 1. Since each Si is four-fold coordinated one can get the maximum possible number of rings per Si to be 6. In our case of SiSe_2 glass we found this number to be 5.83.

The analysis of the integrand in Eq. 3 shows that the relevant distances for the appearance of the FSDP ($q=1.35 \text{ \AA}^{-1}$) should be respectively 6.0 and 10.5 $\text{\AA}$ and at these distances precisely we have peaks on $g_{\text{Si-Si}}(r)$ (Fig. 2). In order to establish a relation between those distances and rings, we calculated the distribution of distances on rings, shown in Fig. 6 only for the Si-Si correlation. One can see that only rings of size above 6 have distances in the range of 10 $\text{\AA}$, while for the peak at 6 $\text{\AA}$ rings of size 4, 5 and 6 also contribute.

4. CONCLUSION

Besides the minor discrepancy in the position of the FSDP, the present work shows most of the observed features in the neutron static structure factor and several interesting and useful ways available for

analyzing the structure of the system. Presently we are in the process of including in the effective interaction potential a three-body term. We believe this improvement will bring the FSDP in the experimentally observed position.

ACKNOWLEDGEMENTS

G. A. A. would like to acknowledge the financial support from CAPES (Post-Graduate Education Federal Agency-Brazil) and the hospitality of the Materials Science Division at Argonne National Laboratory.

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Figures Captions

Figure 1 - The effective interaction potentials between different particles in the SiSe_2 system.

Figure 2 - Partial pair distribution function for Si-Si, Si-Se and Se-Se at $T=335$ K. The dotted lines are the coordination numbers obtained by integrating the corresponding $g_{\alpha\beta}(r)$.

Figure 3 - Bond-angle distributions, calculated for fifty configurations. The cutoffs were chosen from the coordination shells of Fig. 1, 4.6, 3.0 and 5.2 Å, respectively for Si-Si, Si-Se and Se-Se.

Figure 4 - Neutron static structure factor for SiSe_2 glass at $T=335$ K. The continuous line is the MD result while the circles are from the neutron diffraction experiment [1].

Figure 5 - Partial static structure factor for Si-Si, Si-Se and Se-Se. The main contribution for the first sharp diffraction peak (FSDP) comes from the Si-Si correlations and to a lesser extent from the Si-Se.

Figure 6 - Distribution of distances in rings of different sizes. A N-fold ring has N atoms of Si and an equal number of Se atoms.

Table 1 - Distribution of Rings

RINGS	2	3	4	5	6	7	8	9
Number	120	480	2920	5540	9060	5480	1600	60
Number per Si	0.03	0.11	0.67	1.28	2.10	1.26	0.37	0.01

Fig. 1

FIG. 2

Fig. 3

Fig. 4

FIG. 5

FIG. 6