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Realistic models of binary glasses from models of tetrahedral amorphous semiconductors

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We present an approach for modeling binary glasses beginning with models of tetrahedral amorphous semiconductors and report models of glassy $GeSe_2$, $SiSe_2$, SiO_2, and $GeSe_4$. The topology of our models are analyzed through partial pair correlations and static structure factors. Structural properties, including the first sharp diffraction peak, electronic and vibrational properties are all in agreement with experiment. Our approach is simpler and faster than traditional melt-quench simulations and emphasizes the importance of correct topology of starting structure for successful modeling.

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Amorphous semiconductors and glasses are important materials employed in a wide variety of applications such as optical storage devices, solar cells, devices requiring photosensitive materials, and the programmable metallization cell (PMC).[1] The behavior of these systems depends critically on the network topology of the materials. To produce realistic models, it is now conventional to use the methods of ''first principles'' simulation. Most commonly, one employs the ''cook and quench'' technique, which consists of disordering the crystalline phase at high temperature so that the system ''forgets'' its crystalline origin, equilibrating a liquid, then quenching it, and finally performing annealing cycles to bring the system to a local energy minimum state. Although the ''cook and quench'' technique can succeed for certain disordered materials (usually for stoichiometric compositions), it does a rather poor job of making models for general composition.[2,3] We have found it to be useful to include primitive *a priori* information about the chemical order and coordination in model construction.[2,4] This paper demonstrates the utility of such an approach for several binary glasses. The use of such starting points for *ab initio* modeling puts the simulation in the ''right part'' of configuration space (which is of extremely large dimension and complexity). We believe that this ''hunting in the correct subspace'' is needed for current simulations with their few-several picosecond time scales (with consequent severely limited access to configuration space). There is a pressing need for successful schemes for modeling disordered materials of arbitrary composition.

There have been remarkable successes in modeling the structure of column IV (Ge and Si) amorphous materials using the ''WWW'' methods after the authors Wooten, Weaire, and Winer.[5] The WWW approach is based upon particular bond switching events in conjunction with a Metropolis algorithm, Keating potentials (classical springs), and the constraint that atoms are four coordinated. Such models agree not only with the static structure factor, but the electron and phonon density of states as well.[3,6] In addition, we have seen that small (up to 512 atom) models are very close to a minimum for the density functional local density approximation (LDA) energy functional.[7] The method has been generalized to model crystal-amorphous interfaces, and paracrystalline Si.[8] The success of the method rests upon two facts: (1) inclusion of valuable *a priori* information (a constraint that *a*-Si should be four coordinated) and (2) a bond-switching process which appears to be a dominant process in *a*-Si.[9] It is notable that a very naive potential is adequate when the simulation is performed with suitable *a priori* information.

For some of the simulations reported we used FIREBALL, a density functional code in the LDA developed by Sankey and co-workers.[10] This is an approximate *ab initio* local density approach to electronic structure, force and dynamical simulation derived from density functional theory using the Harris[11] functional and a minimal basis set. Because the code employs the Harris functional, no self-consistent field iterations are required, which is of great benefit to the code's efficiency, which is a relevant point for glassy materials which require the use of large supercell models.[12] The basis set is minimal (for these systems, one *s* and three *p* slightly excited pseudoatomic orbitals per site or ''single zeta'' in the language of quantum chemistry). In its original form[10] only weakly ionic systems may be treated; self-consistent versions have been developed recently.[13] These approximations perform exceptionally well for chalcogenide systems.

The other code (in this paper used for silica) is SIESTA,[14] which has broad flexibility with respect to basis set, density functional, and simulation regime. We employed SIESTA for silica because of concerns about the extreme ionicity of the material, and also to easily check the importance of density functional, basis set and spin polarization. In the end, we found that relatively simple approximations (self-consistent LDA and a single zeta basis) was adequate. Even using soft pseudpotentials, we found that a 150 Ry cutoff was needed for evaluation of the multicenter matrix elements.

We made models of $GeSe_2$, $SiSe_2$, and SiO_2 glasses by starting with a defect-free (fourfold coordinated) 64 atom supercell model of *a*-Ge made with the WWW method.[5,15] Characteristic of an amorphous column IV material, this model has bond angles tightly centered on the tetrahedral angle, and has a topology presumably unrelated to g-$GeSe_2$, g-$SiSe_2$, and g-SiO_2. We decorated all the IV-IV bonds with a bond-center VI, and rescaled the coordinates to the experimental density of g-$GeSe_2$, g-$SiSe_2$, and g-SiO_2, respectively. The 192 atom models of g-$GeSe_2$ and g-$SiSe_2$ were then quenched with FIREBALL to the nearest minimum. The 192 atom model of g-SiO_2 was relaxed with SIESTA. We name this scheme ''decorate and relax.'' The central point of

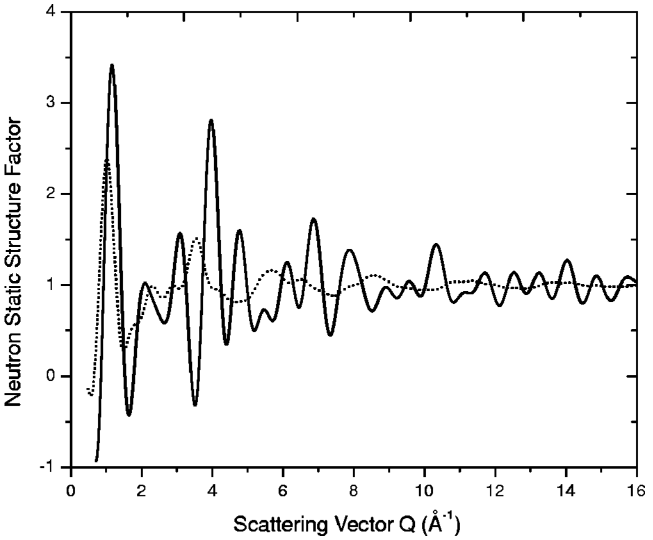

FIG. 1. Calculated total neutron structure factor $S(Q)$ of unrelaxed "decorated" glassy GeSe$_2$ (dotted line) and unrelaxed "decorated" diamond GeSe$_2$ (solid line). We used scattering lengths of $b_{\mathrm{Ge}}=8.185$ and $b_{\mathrm{Se}}=7.970$ fm.

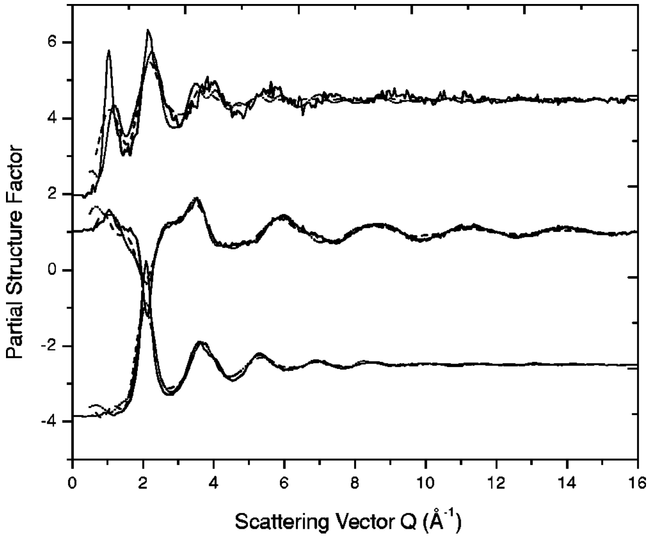

FIG. 2. Partial structure factors $S(Q)$ for glassy GeSe$_2$. The solid curves are from experiment (see Ref. 18), the dashed curves are from the "cook and quench" model (see Refs. 20,21), and the fine dotted curves are from the decorated WWW model (see text).

this paper is that the resulting models are in some ways superior to the best models in existence, are remarkably easy to generate, and preliminary work with Chubynsky and Thorpe suggests that the approach may be extended to off-stoichiometry compositions. Such networks have been introduced and explored by Chubynsky and Thorpe[16] to study the vibrational excitations of chemically ordered networks. Vink and Barkema have also explored some related methods in silica.[17]

The decorated models have general similarities and origins that we illustrate with the case of GeSe$_2$. In Fig. 1 we report the static structure factor for the unrelaxed decorated diamond and decorated WWW *a*-Ge. In both models we note the presence of a strong, sharp prepeak in $S(Q)$. In the "unrelaxed decorated diamond" model, the so called first sharp diffraction peak (FSDP) arises from the $\langle 111\rangle$ Bragg peak of the structure. This prepeak is very similar to the prominent FSDP feature of glasses. The existence of this peak in both models reveals that our starting models already exhibit the intermediate range order associated with the FSDP. Relaxation tunes the topology of the models in order to give the topology and chemistry suited to the particular glass. Other interesting properties of our models are that all have large state-free optical gap consistent with the material under study and the well known limitations of LDA to estimate the gap. The relaxation is substantial enough to create small amounts of chemical disorder and both edge and corner sharing tetrahedra in GeSe$_2$ and SiSe$_2$.

The structure of these models are analyzed by computing the partial Faber-Ziman structure factors. In preliminary work, we compared the results for the Faber-Ziman structure factors $S(q)$ vs experiment,[18,19] the earlier model of *g*-GeSe$_2$ (Refs. 20,21) and the new model (Fig. 2). The decorated model is at least as good as the previous model and comparable to the models of Massobrio and co-workers.[22,23] While the model has strong similarities manifested in the partial structure factors, and essentially similar topological/chemical ordering a key difference of the "decorated" model is the persistence of correlations in $S(q)$ beyond 10 Å^{-1}in unique and pleasing agreement with experiment, whereas the earlier model displays a more rapid decaying amplitude for large q (for an expanded scale, see our preliminary report[24]). Our interpretation of this is that the cook and quench model was too "liquid like" — precisely the kind of artifact one might expect from rapidly quenching a liquid on the computer.[25] The new model has 86% heteropolar bonds, with the homopolar bonds Se-Se (13.5%), except for a single Ge-Ge bond (0.5%). Ge was 78% fourfold, 19% threefold, and 3% twofold, numbers quite consistent with the earlier model. We also computed the vibrational and electronic states densities (EDOS) and found them to be very similar to the earlier model of Cobb.[21] The peaks in the EDOS are discussed in Table I and plotted in Fig. 3.

"Decorate and relax" was also used to generate a model of *g*-SiO$_2$. The properties of our model have been studied through the neutron static structure factor and the partial pair-correlation function. In Fig. 4 we illustrate the real-space partial pair correlation function and compare to experiment.[28] The agreement between the experiment and theory is quite good. The position of the first peak in $g_{\mathrm{SiO}}(r)$ gives the Si-O bond length to be 1.62 ± 0.02 Å . The corre-

TABLE I. The positions of the A_1, A_2, A_3 and B peaks in the EDOS of our "decorated" model of *g*-GeSe$_2$ compared to experimental (Ref. 26) and "cook and quench" (Ref. 21) results.

(eV)	A_1	A_2	A_3	B
Decorated	-1.36	-2.8	-4.5	-7.2
Experiment	-1.38	-3.0	-4.6	-7.8
Cook and quench	-1.4	-2.7	-4.6	-7.0

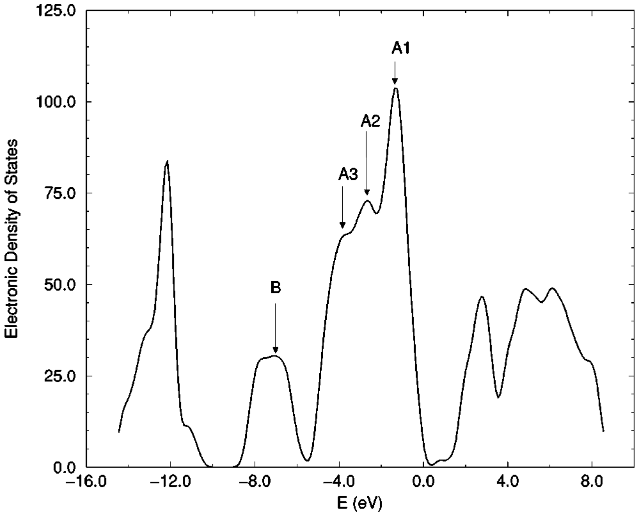

FIG. 3. Electronic density of states of 192 atom decorated and relaxed model of g-GeSe$_2$. The letters indicate peaks discussed in Table I.

sponding experimental value from neutron-diffraction data[28] is 1.61±0.05 Å . The nearest-neighbor O-O distance from Fig. 4 is 2.65±0.05 Å and the corresponding experimental value, inferred from neutron-diffraction data, is 2.632 ±0.089 Å . By taking the Fourier transformation of the pair-correlation function we compute the neutron static structure factor $S_N(Q)$ that can be directly compared to its experimental counterpart.[27] The total static structure factor of our model, together with the one obtained by neutron diffraction experiments[28] are presented in Fig. 5. Our results are again in reasonable agreement with experiment. The position of the FSDP of our new ‘‘decorated’’ model coincides with the experimental one. The system has no homopolar bonds, as one would expect from the chemistry of silica.

We extended the method to g-SiSe$_2$. The properties of our ‘‘decorated’’ model is studied through the neutron static structure factor and the partial pair-correlation function. In Fig. 4 we present the real-space partials pair correlation function of our model. There is good agreement between our simulated results and the earlier model.[29] The sharp peak in the pair correlation function $g_{\mathrm{SiSe}}(r)$ is due to the largely predominant heteropolar Si-Se bonding. In $g_{\mathrm{SiSi}}(r)$ the peak at 2.4±0.05 Å is due to Si-Si homopolar bonds. The main peak in the $g_{\mathrm{SeSe}}(r)$ stems from the intratetrahedral second neighbor Se-Se distances while the small peak at 2.4 Å is indicative of homopolar Se-Se bonding. The calculated neutron scattering strucure factor (Fig. 5)shows very good agreement with experiment.[30] The calculations for the peak position agree very well with the experimental results.

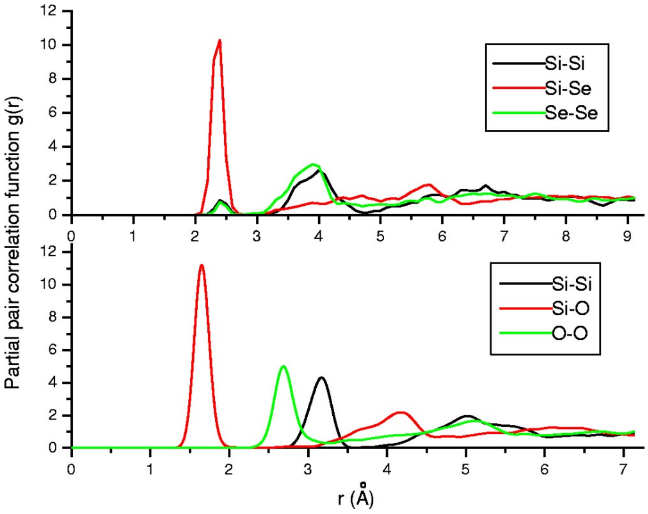

FIG. 4. Partial pair distribution functions $g_{\alpha_\beta}(r)$ vs r in g-SiSe$_2$ (top panel)and in g-SiO$_2$ (bottom panel).

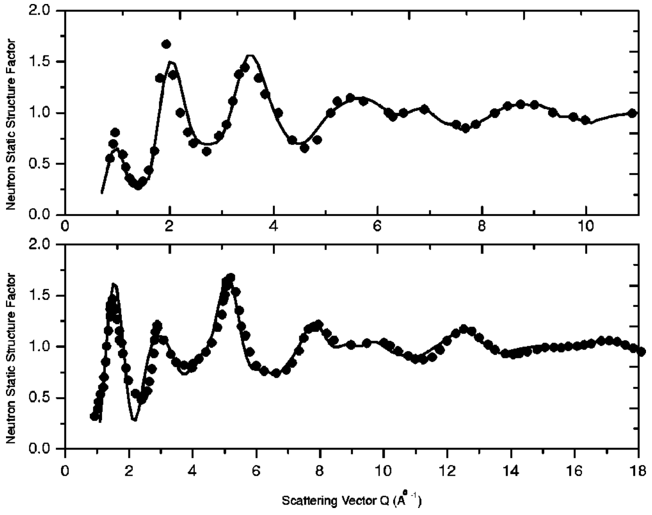

FIG. 5. Top: Calculated total neutron static structure factor $S(Q)$ of glassy SiSe$_2$ compared to experimental data from Ref. 30 (filled circles). Bottom: Calculated total neutron static structure factor $S(Q)$ of glassy SiO$_2$ compared to experimental data from Ref. 28 (filled circles). We used scattering lengths of $b_{\mathrm{Si}}=4.149$, $b_{\mathrm{Se}}=7.970$, and $b_{\mathrm{O}}=5.803$ fm.

Collaborative work with Chubynsky and Thorpe suggests that the method might be readily extended to nonstoichiometric glasses. These workers provided us with a decorated and unrelaxed model of glassy g-GeSe$_4$ based as before on a WWW model, but with additional Se added at random. In Fig. 6 we compare the neutron static structure factor for the glassy GeSe$_4$ with the experimental data for the corresponding liquid[31] [we could not locate $S(q)$ for the glass]. Comparing our VDOS with experiment obtained by neutron inelastic scattering,[32] the spectrum exhibits the same features (Fig. 7). Three bands can be distinguished: a low energy acoustic band involving mainly extended interblock vibrations and a high energy optic band consisting of more localized intrablock vibrations. The two main bands are clearly separated by the tetrahedral breathing (A_1-A_{1c})band.

The neutron weighted total structure factor $S(Q)$ and the corresponding partial pair correlation function have been computed for the relaxed decorated structures and compared with the experimental neutron diffraction results. Excellent agreement is found with the experimental data in the high Q region above 5 Å^{-1} (i.e., within the experimental errors) for all the $S(Q)$ indicating that the short range order is well reproduced for all configurations. In the low Q region, how-

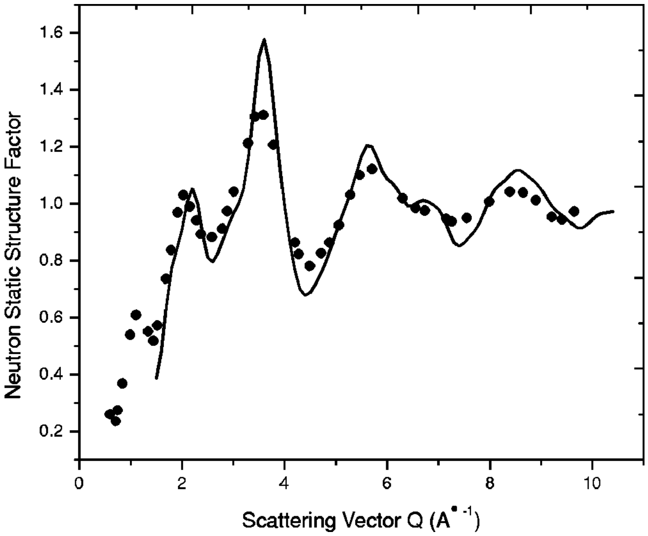

FIG. 6. Calculated total neutron static structure factor $S(Q)$ of glassy $GeSe_4$ compared to experimental data of liquid $GeSe_4$ from Ref. 31 (filled circles).

ever, there are small deviations from the experimental data. The peak amplitude and the position of the FSDP in the glasses are well reproduced. All models presented have a clear optical gap free of defect states. The key point is that with a simple idea we were able to generate models of IV-VI_2 glasses close to the best "cook and quench" models, with some additional positive features such as a proper asymptotic behavior in $S(Q)$ for large Q. It spares us from expensive calculations of cook and quench technique (many phases with many time steps each). Overall the decorated scheme is much faster than the traditional methods (at least 10 times faster for a give interatomic interaction). To the extent that no scheme including "cook and quench" can be claimed to mimic the *physical* process of glass formation (because of the profoundly limited non-ergodic sampling of configuration space), this method should be evaluated by its success in reproducing the known experimental information. The models of $SiSe_2$ and SiO_2 will be described more fully in subsequent work.

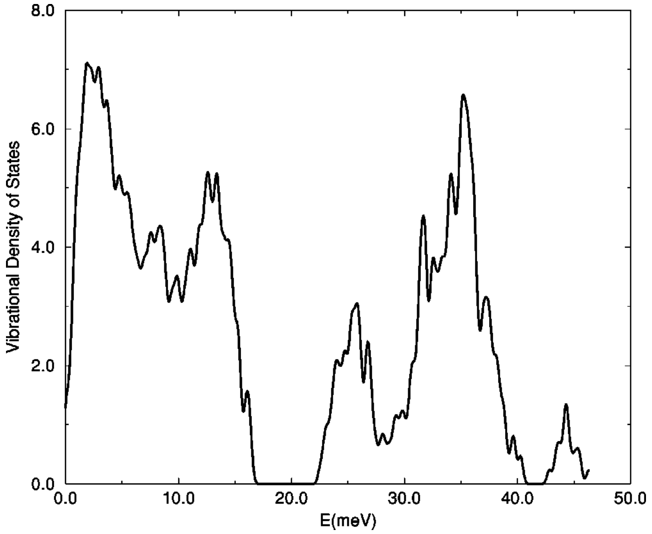

FIG. 7. Predicted vibrational density of states for glassy $GeSe_4$.

Note added in proof. Recently, we employed this scheme to generate a 648 atom model of silica, and find that $S(q)$ is significantly improved near q=2.0 Å^{-1}.

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