

Direct Molecular Dynamic Simulation of Light-Induced Structural Change in Amorphous Selenium

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An amorphous selenium network structure was constructed by combination of a lattice random walk and *ab initio* molecular dynamic (MD) simulation. The static structure factor, pair correlation function, and vibrational and electronic density of states simultaneously agree with experiment. For the first time, we study structural rearrangement due to light-induced changes in occupation. The predictions of the Kastner *et al.* valence alternation model are essentially confirmed, and new features of the rearrangement are elucidated. The structural rearrangements are less local than in simple models.

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The unique photoelectronic properties of *a*-Se makes it an ideal material for photoreceptor in the photocopying process [1] and photoconductor in digital radiography [2]. Ample evidence exists that chalcogenide materials contain defect states. This follows from photoluminescence measurements, photoconductivity, a pinned Fermi energy, and other observations. But in contrast to amorphous column IV materials, there is no ESR signature of their presence. To explain this, Anderson [3] proposed a model in which a phonon coupling gives rise to a negative Hubbard energy U_{eff} to doubly occupy one-electron levels. An important extension of this idea by Street and Mott [4] argued that the negative U_{eff} in chalcogenides arises from lattice distortions at dangling-bond sites, which are unstable towards formation of charged defect centers with entirely paired spins. Subsequently, Kastner, Adler, and Fritzsche [5] used simple chemical-bonding arguments to suggest that the lowest-energy neutral defect is a threefold-coordinated site which is unstable towards the creation of different positively charged and singly negatively charged threefold-coordinated atoms, valence alternation pairs, or VAP's.

Although the VAP model was successful in explaining most of the properties of lone-pair semiconductors, there has so far been no *realistic* calculation to support the existence of the negative U_{eff} and valence alternation in *a*-Se. The difficulty stems from two considerations. First, earlier calculations [6] imposed defects on Se chains which are taken to be the *a*-Se structure. Those artificial defects bear limited resemblance to real *a*-Se. Second, previous *ab initio* molecular dynamic (MD) calculations [7] yielded too many coordination defects so that the defects cannot easily be analyzed as isolated entities. The defect-defect interaction causes an unphysical reduction in the localization of the defect wave function which affects interatomic forces and their sensitivity to occupation changes.

In this Letter, we report the first *ab initio* study of light induced effects for *a*-Se. Our study of these important properties is made possible by use of *ab initio* MD in conjunction with a new algorithm for obtaining a model

of *a*-Se. The resultant *a*-Se structure contains only one VAP defect and the static structure factor, pair correlation function, electronic and vibrational densities of states are in good agreement with experiments [8,9]. Bond breaking and recombination of the structure due to optical excitation are directly simulated using this model. The signatures of photostructural change are in impressive agreement with the VAP model and recent experiment, though the process is less local than one usually imagines with the VAP model.

We used the program of Demkov, Ortega, Sankey, and Grumbach [10], "Fireball96" to construct our network and use approximate Kohn-Sham orbitals as if they were "genuine" electron states. For the details of this method, the reader is referred to Refs. [10,11]. The method has been used previously to form a small model of *a*-Se [12]. The use of Kohn-Sham states is not fundamentally justified, though there are many computations that show that this can be useful [13]. Indeed, it is of some independent interest that these approximate and generously interpreted orbitals capture the physics quite well as we show below. We think this is because the effects we report here do not depend on particularly subtle features of the electronic structure.

Our approach to simulating *a*-Se involves two steps. We use a new algorithm to construct the amorphous structure for a large (216-atom) model. Realizing that the chain structure is the major component for *a*-Se, we build a long chain on a simple cubic lattice random walk as the initial configuration for our model. For our 216-atom model, we first obtained two chains with 199 atoms and 17 atoms as our initial model. The bond angle between two neighboring members of the chain is 90° and bond length is 2.15 Å. Then, a standard *ab initio* MD "cook and quench" procedure was applied to this initial structure. It is quite interesting that a very long chain (159 atoms), two shorter chains (28 and 24 atoms, respectively), and one 5-atom ring appear in this 216 atom model. The long chain connects with a shorter chain at a three-coordinated defect. The appearance of a 5-atom ring in this model gives additional strong evidence that coexisting long chains and rings

is the basic structure of a -Se, as we also saw in our 64 atom calculation [12]. This is in pleasing agreement with experiment [14].

To assess the validity of our 216 atom model a -Se structure, in Fig. 1 we compare our computed pair distribution function $g(r)$, static structure factor $S(Q)$, and vibrational density of states with experiment where available. The calculated pair correlation function shows pleasing agreement with experiment [8] and peak positions agree closely with Refs. [15,16].

As shown in Fig. 1(b), the static structure factor $S(Q)$ is in reasonable agreement with measurements taken from Ref. [8]. The location of principal peaks and intensities is close to the measured ones and even the oscillation between the third and fourth peaks in the experimental curve is exactly reproduced. The discrepancy in the first peak probably arises mostly from finite-size artifacts as we have tested in detail, though one cannot rule out that an extended exploration of configuration space might lead to closer coincidence. We stress, however, that the overall agreement is very satisfactory.

The vibrational density of states (VDOS) of a -Se has been studied using inelastic neutron scattering by Kamitakahara *et al.* [9], and in Fig. 1(c) we compare our VDOS with their experimental measurement. The agreement between the experiment and our simulation is excellent. Even the spectrum at the 20–30 meV region is reproduced in our simulation. We will describe these modes elsewhere [17]. The lowest energy modes are extended.

We stress that our model is in *uniform* agreement with structural, vibrational, and electronic measurements. For

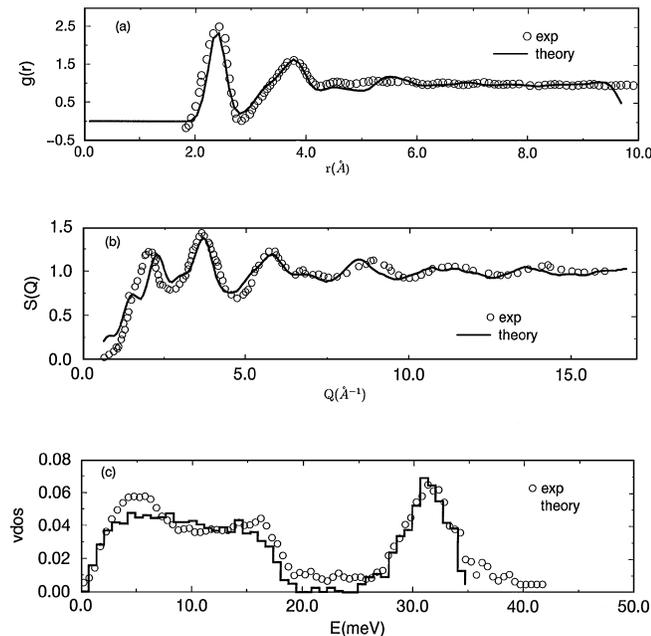


FIG. 1. Comparison between experiment and theory: (a) pair-correlation function $g(r)$; (b) static structure factor $S(Q)$; (c) vibrational density of states

comparison, we also discuss light-induced effects in our earlier 64-atom model [12]. In our 64-atom model [12], there is only one “intimate” VAP (IVAP). The localized states at the top of the valence band arise almost solely from the singly coordinated sites. The localization at the conduction band edge is predominantly on the threefold site and its nearest neighbors. The important observation for the IVAP defect in the 64-atom model is that the singly coordinated defect is more localized. This agrees with the early tight-binding calculation by Vanderbilt and Joannopoulos [6]. The density of electron states and the localization of defect eigenvectors of our 216-atom model [17] is similar to that of the 64-atom model [12].

The photostructural changes in chalcogenide glasses have been the subject of numerous investigations but the microscopic mechanism of such changes still remains unclear. If a model contains too many defects, it is hard to disentangle the structural change induced by optical excitation or other factors such as thermal disorder, etc. Our models contain the fewest defect sites and, as such, provide a suitable starting point for modeling the light-induced structural changes in a -Se.

We use the method developed by Fedders, Fu, and Drabold [18] to simulate the light-induced structural change. First, we transfer the electron occupied at the highest occupied molecular level (HOMO) to the lowest unoccupied molecular level (LUMO) [19]. We imagine this change in the charge of a localized state as a simple model of an electron ejected from the valence band to the conduction band by a photon. Then we let the system evolve freely without either adding or taking away energy. We found that the initial local disturbance of the atoms kept propagating outward. We let the supercell evolve for 400 fs and observed how the topology changed during this optical excitation. Then we quenched the model to $T = 0$ K. Other times (200 and 600 fs) were tested; the former led to no photostructural change, and the latter to the same structure as 400 fs. A fuller study of this point is under way. We also repeated all this with constant temperature MD (300 K) and found that the results were essentially identical.

Figures 2(a) and 2(b) reveal the structural change during this simulation for the 64-atom model. We found that the one-coordinated defect was converted to a three-coordinated defect, and the structural change was somewhat nonlocal. Adjacent to the initial IVAP, two bonds were broken and two of the resulting defect atoms formed a new bond. One of the new defects converted to a three-coordinated defect and the other remained a one-coordinated defect. The fact that the original one-coordinated defect site was converted to the three-coordinated defect site is just another prediction by the VAP model. Since the negatively charged one-coordinated defect atom becomes neutral C_1^0 by the optical excitation, this C_1^0 is not very stable and tends to convert to C_3^0 . The change in the other region is also easy to

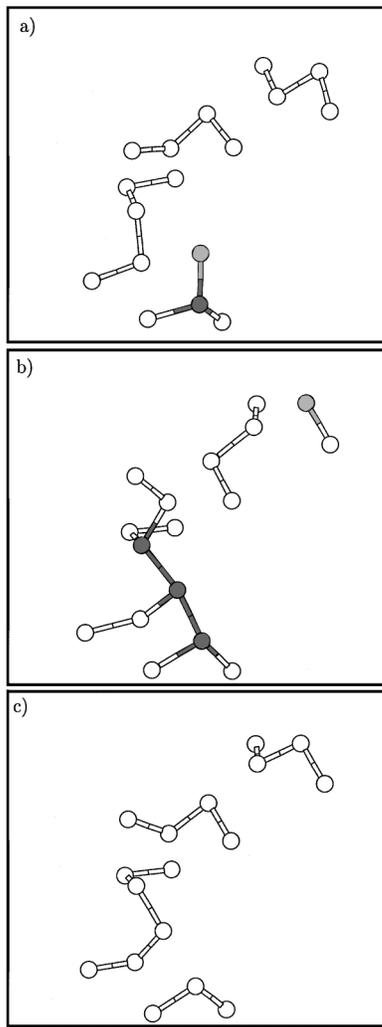


FIG. 2. Simulation of optical excitation for the 64-atom model [12]. Only affected atoms are shown: (a) before the optical excitation; (b) (nonequilibrium state) at the end of the optical excitation; (c) after quenched back to the energy minimum. The grey scale in this figure represents the coordination: white, two-coordinated; grey, one-coordinated; black, three-coordinated.

understand if we assume the C_3^0 defect to be the most probable neutral defect in *a*-Se. *The local disturbance in the defect region will first cause bond breaking, producing some C_1^0 defects, and these C_1^0 defects have a propensity to convert to C_3^0 defects.* Thus, it appears that the key to understanding the structural change by optical excitation is to admit the assumption, C_3^0 being the most stable defect in *a*-Se. This is an important assumption in the VAP model by Kastner *et al.* [5]. We computed atomic charges using a Mulliken analysis and found that onefold atoms are negatively charged (depending somewhat on the local environment, a charge of $(0.07-0.1)e$ is transferred); threefold atoms are positively charged and by a similar amount. Two-coordinated sites have a typical charge of magnitude less than $\approx 0.02e$. We performed tests with DMol [20] and found semiquantitative agreement

with Fireball96 charges for a 17 atom Se molecule with an IVAP.

Figures 3(a) and 3(b) show the photostructural change for the 216-atom model. As for the 64-atom model, the one-coordinated defect converts to a three-coordinated defect. A majority of photocreated defects are three coordinated suggesting that these are the most probable neutral defects in *a*-Se. It is interesting that three-coordinated defects tend to cluster together. This phenomenon was also observed in the calculation of Hohl *et al.* [7]

We have found that in both the 64- and 216-atom models, the HOMO and LUMO levels move into the middle of the gap during the photoexcitation process. This is readily explained by the VAP model, and the associated states are localized on miscoordinated neutral defects.

The final step is to deexcite the electron and then quench the sample. It is striking that all the defects disappear after we quench the system to an energy minimum for the 64-atom model. This structural change is shown in Fig. 2(c). This structural change then reveals one possible

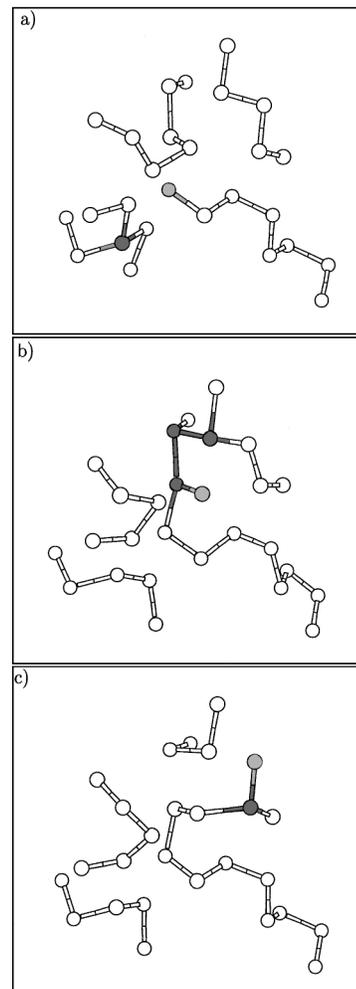


FIG. 3. Simulation of optical excitation for the 216-atom model. Same grey scale as in Fig. 2.

outcome, an interesting “optical annealing,” rather akin to light-induced crystallization. For the 216-atom model, as shown in Fig. 3(c), the original VAP defect disappears, and a new IVAP defect is formed.

We repeated the same MD simulations for the above processes without optical excitation. We used the same parameters, time step, and quench rate except that we did not remove the electron from our system. After, we let the system freely evolve for 400 fs and quenched it back. The structure is the same as the original structure. This indicates that the structural change in our first simulation is really induced by optical excitation.

Our structural model gives a description of the microscopic *a*-Se network of unprecedented quality, as evidenced by the comparison with experimental data where available. A recent generalized gradient approximation (GGA) calculation [21] gave a better agreement with experiment for *l*-Se. So, it is proposed by Kirchoff *et al.* that the GGA is essential to obtain the proper nearest-neighbor distance. We have verified that our Hamiltonian gives a dimer bond length of 2.18 Å which is close to an experimental length 2.17 Å. We noticed that the improvement from the GGA calculation by Kirchoff *et al.* is due to decreasing the depth of the first minimum in the pair correlation function $g(r)$ which is much higher in the local-density-approximation calculation as well as in the Hohl and Jones calculation. To verify this point, we did two studies. First, we use a steepest descent quench to fully relax Hohl and Jones’ network with our Hamiltonian [10]. The quenching decreases the first minimum of $g(r)$ and the resulting $g(r)$ is in improved agreement with experiment. The relaxed model only contains a bonded $C_3 + C_1$ IVAP pair and a pair of C_3 and C_1 (VAP). Second, we used the powerful first principles MD program, SIESTA [22], to relax our 64-atom model. We included the GGA and pseudopotential core correction with a double-zeta polarized basis to quench our 64-atom model. However, we did not observe the improvement to the structural properties of our model by this more expensive calculation.

One additional implication of this work is that neutral C_3^0 is easy to form. These C_3^0 defects may be frozen in the material if the system is quenched very quickly. This may explain why most of the theoretical calculation and some experiment showed that the coordination number for *a*-Se is slightly larger than 2.

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- [1] J. Mort, *Phys. Today* **47**, No. 4, 32 (1994).
 - [2] J. Rowlands and S. Kasap, *Phys. Today* **50**, No. 11, 24 (1997).
 - [3] P. W. Anderson, *Phys. Rev. Lett.* **34**, 953 (1975).
 - [4] R. A. Street and N. F. Mott, *Phys. Rev. Lett.* **35**, 1293 (1975).
 - [5] M. Kastner, D. Adler, and H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
 - [6] D. Vanderbilt and J. D. Joannopoulos, *Phys. Rev. B* **22**, 2927 (1980).
 - [7] D. Hohl and R. O. Jones, *Phys. Rev. B* **43**, 3856 (1991).
 - [8] R. Bellissent, *Nucl. Instrum. Methods Phys. Res.* **199**, 289 (1982).
 - [9] W. A. Kamitakahara (private communication).
 - [10] A. A. Demkov, J. Ortega, O. F. Sankey, and M. Grumbach, *Phys. Rev. B* **52**, 1618 (1995).
 - [11] Otto F. Sankey and D. J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989); Otto F. Sankey, D. A. Drabold, and G. B. Adams, *Bull. Am. Phys. Soc.* **36**, 924 (1991).
 - [12] X. Zhang and D. A. Drabold, *J. Non-Cryst. Solids* **241**, 195 (1998).
 - [13] F. Mauri and R. Car, *Phys. Rev. Lett.* **75**, 3166 (1995); J. Song *et al.*, *Phys. Rev. B* **53**, 8042 (1996); O. Pankratov and M. Scheffler, *Phys. Rev. Lett.* **71**, 2797 (1993); for transport, G. Galli *et al.*, *Phys. Rev. B* **42**, 7470 (1990).
 - [14] B. W. Corb, W. D. Wei, and B. L. Averbach, *J. Non-Cryst. Solids* **53**, 29 (1982).
 - [15] E. H. Henninger, R. C. Buschert, and L. Heaton, *J. Chem. Phys.* **46**, 586 (1967).
 - [16] R. Kaplow, T. A. Rowe, and B. L. Averbach, *Phys. Rev.* **168**, 1068 (1968).
 - [17] X. Zhang and D. A. Drabold (unpublished).
 - [18] P. A. Fedders, Y. Fu, and D. A. Drabold, *Phys. Rev. Lett.* **68**, 1888 (1992).
 - [19] We promoted either one or two electrons from the HOMO level; relaxations were similar. We report the two electron case here. The single electron promotion is probably best handled at the LSDA level.
 - [20] For example, B. Delley, in *Modern Density Functional Theory: A Tool for Chemistry*, edited by J. M. Seminario and P. Politzer, Theoretical and Computational Chemistry (Elsevier Science Publishers, Amsterdam, 1995), Vol. 2.
 - [21] F. Kirchoff, G. Kresse, and M. J. Gillan, *Phys. Rev. B* **57**, 10482 (1998).
 - [22] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, *Int. J. Quantum Chem.* **65**, 453 (1997).