

SIMULATION OF THE RESPONSE OF AMORPHOUS SELENIUM TO LIGHT

Xiaodong Zhang and D. A. Drabold
Department of Physics and Astronomy, Ohio University
Athens, Ohio 45701 USA. www.phy.ohiou.edu/~drabold

Received 20 September 2000

We investigated the physical mechanism of dynamical bond formation, light-created defect centers and light induced electron spin resonance for Se chains and a realistic model of amorphous selenium by ab-initio molecular dynamic simulation. It is found that the Coloumb interaction between light-created charge centers plays the key role in the bond breaking, switching and reconstruction in Se chain and a-Se under the light irradiation.

1. Introduction

For chalcogen glasses, there are midgap defects but their nature is very different than amorphous column IV midgap states. Due to the defects, unpaired spins near the Fermi level E_F are expected, but no ESR indicates their presence. In order to explain these apparently contradictory observations, the concept of defects with negative correlation energy “negative U” favoring the formation of doubly occupied states was suggested¹. Recent experiments on optically induced ESR by Kolobov et al.² gave strong support for the negative U. They observed that the ESR-active defect centers were created by breaking the inter-chain bonds under photo-excitation. They also observed fast and slow ESR signals for the film previously irradiated for several hours and then annealed at low temperature.

Our previous work^{3,4} on light induced structural change on a-Se shows that the major structural change for a-Se occurs near the defect site and that the photo excitation will anneal the defect or cause defect diffusion. This work also supports the idea of the “negative U”. The defect sites are most sensitive to light exposure because it is states (near E_F) localized in their vicinity, which suffer light-induced occupation change (and therefore local change in forces). In this paper, we want to further study how defects are created by light excitation. Particularly, we want to link our theoretical molecular dynamics simulation to the recent experiment by Kolobov et al. We first explain the physical mechanism of the dynamic inter-chain bonds formation under the photo-excitation. Then we study how the defect was created by photo-excitation which can help us understand the fast and slow LESR components observed experimentally.

2. Preliminary theoretical considerations

The calculations have been performed by using a local orbital first principles quantum molecular dynamics (QMD) method designed for applications to large systems and implemented in the Fireball package⁵. Numerous recent applications of the technique to a variety of materials problems are reviewed in Ref. 6.

We use two models to study light induced structural change for selenium. The first model consists of two infinite parallel chains of Se. The chain model was constructed by selecting two infinite chains from trigonal Se, breaking the periodic boundary condition perpendicular to the chain direction and relaxing this structure using *ab-initio* MD simulation. The bond angle, dihedral angle and bond distances are consistent with other calculations. The second model is a defect free amorphous selenium model. This 64 atom a-Se model was first constructed by doing “cook and quench” for a random 64 atom Se configuration by *ab-initio* MD simulation. The initial model contains a intimate valence pair (IVAP) defect. The model was further annealed by light excitation and *became a defect free model*^{3,7}.

Photo excitation was simulated by using the same approach as that introduced before^{3,4}. During the MD simulation, we transfer the electron occupied at the highest occupied molecular level (HOMO) to the lowest unoccupied molecular level (LUMO). We imagine this change in the charge (or occupation) of a localized state as a simple model of an electron promoted from the valence band (in this paper just the HOMO level) to the conduction band (LUMO level) by the photon.

3. Results

3.1. Dynamical inter-chain bond formation

The process of the photo-structural change of the parallel chain is shown in Fig. 1. The process can be understood in two stages. The first step is the defect creation process. This process lasts around 250 fs as indicated by Fig. 1a-e. The second step is the process of stabilization of the defect as seen by Fig. 1e-f. The dynamical inter-chain bond formation is clearly seen in Fig. 1b. To our knowledge, this is the first direct simulation to confirm this dynamical inter-chain bond observed in experiment². The dynamical bond formation during the early stage of the photo excitation is contrary to *a priori* intuition. Conventionally, breaking the bond in the chain is expected. Here, we want to explore what physical mechanism makes the dynamical inter-chain bond formed by analyzing the *ab-initio* MD simulation.

The chemistry behind this process can be understood by looking at the charge evolution of the relevant atoms during the photo-excitation. The charges of the atoms are calculated by the standard Mulliken population analysis⁸. The time evolution of the Mulliken charge of relevant atoms during the photo-excitation is shown in Fig. 2. Initially, all the atoms in this two-chain configuration are equivalent. The net effect of random thermal fluctuation and the photo-excitation process,

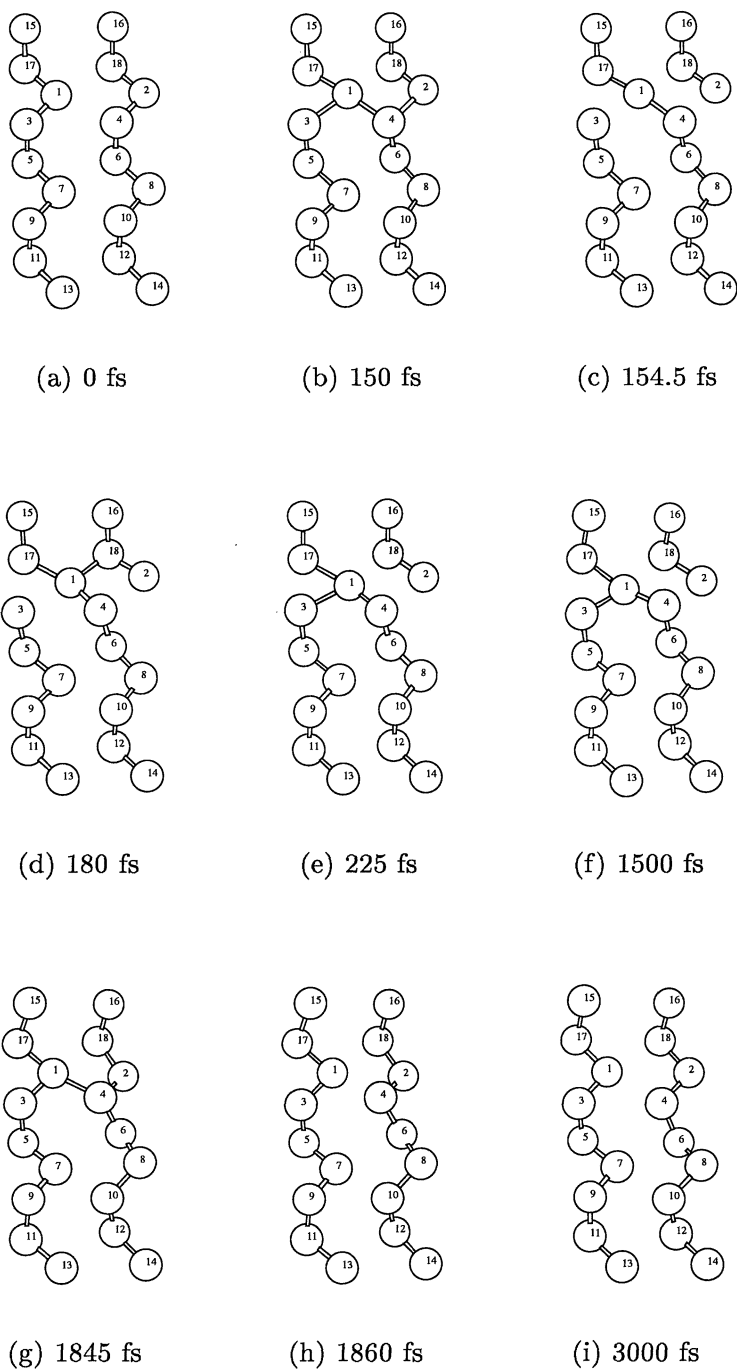


Fig. 1. The simulation of photo structural change of parallel Se chain. We maintain light excitation before 1500 fs, after 1500 fs, we relax the light excited conformation to optimal structure

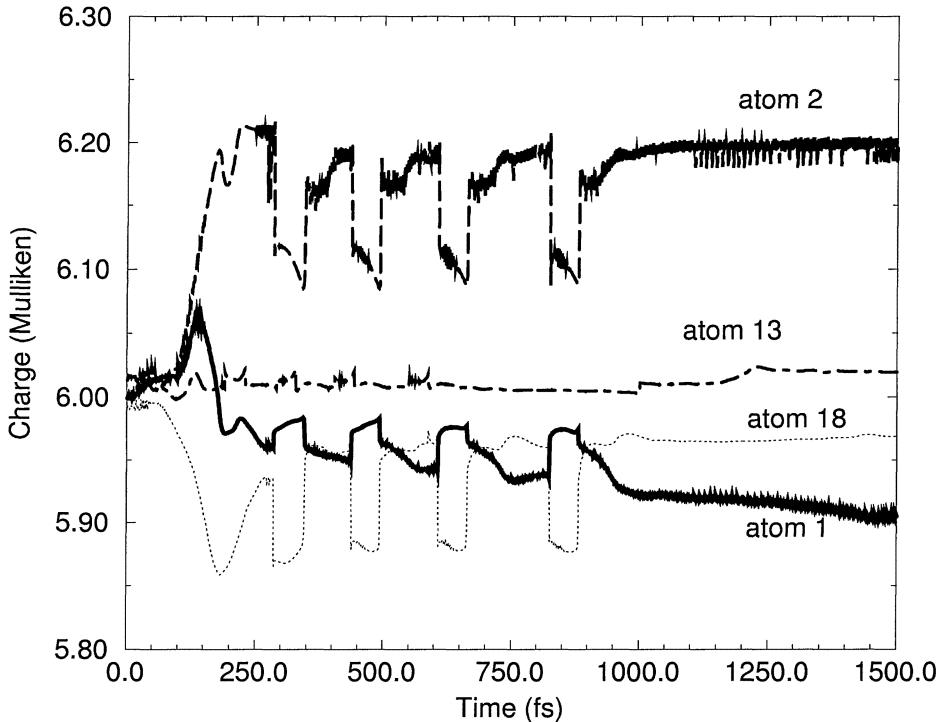


Fig. 2. Time evolution of Mulliken charge for the involved atoms during the photo-excitation. (Parallel chain case). Atom 13 has charge near 6.0 and is shown as a reference atom which was inactive during the simulation. Charges larger than 6 are electron rich, smaller are deficient.

moves the electrons at atom 18 and 17 to atoms 1 and 2. This process can be seen from Fig. 2 at the beginning of the simulation (from 0 fs to 150 fs), where the charge of atom 1 and 2 increase (more negative [electron rich]) and the charge of atom 18 decrease (more positive [electron deficient]). However, with atoms 1 and 2 becoming more negatively charged, atom 18 becomes more positively charged, and the Coulomb interaction between atoms 18 and 1 will attract atom 1 to atom 18. After atom 1 moves close to atom 18, atom 1 is not geometrically equivalent to atom 2. *As atom 1 becomes a three coordinated site due to Coulomb interaction, the role of atom 1 changes after the transfer. As shown in Fig. 2, the charge of atom 2 has a transition around 150 fs. The dynamical bond shown in Fig. 1b is formed around this time. This means that electron charge will move away from atom 1 during the photo excitation process, after atom 1 makes the transition from two- to three- coordination.* So, we can see that the dynamical bond formation is a intermediate process for defect creation by photo excitation. The origin of this dynamical bond is the positive and negative charge centers formed by the photo excitation. The residual Coulomb interaction during the photo-excitation causes atom 1 become three coordinated.

Fig.1b-e shows the reaction $2C_3 \rightarrow C_3^+ + C_1^-$. The two C_3 centers are atom 1 and atom 4 shown in Fig. 1b, and C_3^+ and C_1^- are atom 1 and 2 respectively shown in Fig. 1(f). This dynamical process involves relaxation of the photo-created VAP defect under the condition of the photo-excitation. This relaxation process is also shown in the Fig. 2 from time 150 fs- 250 fs. From time 250 fs-800 fs, we can still see some fluctuation of the charge of those relevant atoms. The photo-excited system is rather stable. It is interesting to observe that the VAP defects are somewhat charged even for the photo-excited system. During the time from 250 fs - 1500 fs, the light excitation persists but the system is stable and no new defects are created.

After we turn off the light, the structure with light created VAP defects takes about roughly the same amount time (after 350 fs) to relax back to the initial structure as the time (around 300 fs as shown in Fig. 2.) spent to create these defects. This can also be observed by tracking the time evolution of the energy of the system. Since the VAP defect created by light is a local bond rearrangement in this simulation, the structural change is reversible. In the real situation, the bond rearrangement is not necessary local and the structural change is also not necessary reversible. We will discuss this in the next section.

3.2. Defect creation by photo excitation in a realistic model

The previous section on light induced effects for a simplified parallel chain model can give us some intuitive physical insight on the physical mechanism of structural change and LESR in a-Se. In this section, we further analyze the light induced ESR in a realistic a-Se model. We use a defect free 64 atom selenium model to study the possible mechanism for the fast ESR component observed experimentally.

Similar to the simulation scheme for the parallel chain, we “turn on” the light for 1.5 ps (maintain the electronic promotion from HOMO to LUMO) and relax the light excited state for 6 ps. Fig. 3 shows the whole process. For the a-Se model, the dynamical bond formed very quickly (60 fs shown in Fig. 3b) . By checking the time evolution of the charge for the atoms, we observe that the extra bond between atom 7 and 10 is formed due to the Coulomb repulsion. The charge transfer due to photo excitation makes atom 1,7,9 and 10 negatively charged. The unbalanced Coulomb interaction between atoms 9 and 10 and between atoms 1 and 7 will propel atom 10 and 7 close each other, making a dynamical 7-10 bond. *Atom 7 prefers to be three coordinated after forming the dynamical bond. Its role in the charge transfer changed. In this time, it gives charge to other atoms rather than taking charge from other sites.* The role change of atom 7 can be seen by time evolution of the charge of atom 7. It initially increases and after 60 fs the charge decreases. The final configuration under the influence of light is equilibrated through forming two charge transfer regions: atoms pair (3,9) and (7,10).

Compared to what happened in the parallel chain, the situation in the a-Se is more complex. Although our initial a-Se model is a defect free model, not all atoms are equivalent in term of their charges. Initially, atom 3 is positively charged and atom sites 7,9 and 10 are slightly negatively charged. The very small charge makes

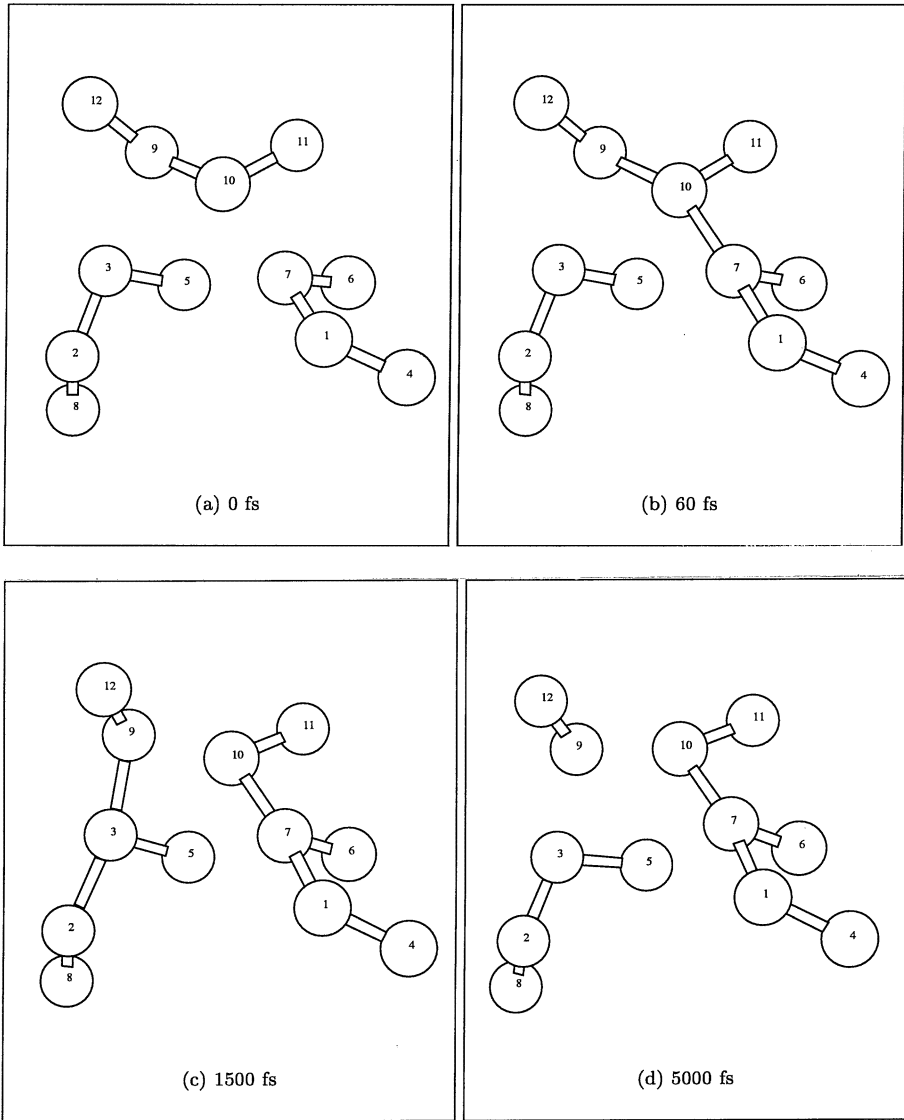


Fig. 3. The simulation of photo structural change in a defect free a-Se model. We do the photo excitation before 1500 fs, after 1500 fs, the structure is relaxed to the optimal structure.

the major bond breaking/rearrangement activity happen near these sites. Atom 3 is a two coordinated site but it behaves like a three coordinate defect due to its positive charge. In amorphous selenium, the light created VAP defects are locally optimized sites. So, even after we turn off the light, those VAP defects still have a chance to survive. The VAP defect in the final structure reflects the fast ESR signal observed in the experiment for the second laser irradiation samples. We also carefully anneal our final structure of a-Se model at higher temperature, we found a carefully annealing scheme can anneal the light created defect away. As a matter of fact, one annealing scheme is the "photo annealing" scheme which was presented in our previous work³.

4. Summary

We presented two simulations to model the LESR recently observed in the experiment: photo-structural change in an infinite parallel chain and photo-structural change in a 64 atom a-Se model. For the parallel chain model, the ESR center is a VAP defect. However, the ESR centers for the a-Se model are two C_3 centers. These centers have all been observed in the experiment. The important observation in our simulation is: the residual Coulomb interaction (attraction or repulsion depending on the environment of those atoms) between the atom sites affected by the light excitation cause the dynamical bond formation; the light created defects are charged defects which is only ESR active under the light excitation; the role of the defect center in the charge transfer will change according to its bonding; the light created defect center will have some possibility to remain in the annealed sample causing the fast ESR signal.

Acknowledgements

This work was performed in part under the auspices of the U. S. NSF under Grant No. DMR 00-81006 and DMR 96-04921. We thank Dr. Jun Li and Professor Himanshu Jain for helpful discussions.

References

1. P. W. Anderson, *Phys. Rev. Lett.* **34**,953 (1975); R. A. Street and N. F. Mott, *Phys. Rev. Lett.* **35**,1293 (1975); M. Kastner, D. Adler and H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
2. A. V. Kolobov, M. Kondo, H. Oyanagi and A. Matsuda, *Phys. Rev. B* **58**, 12004,(1998).
3. Xiaodong Zhang and David Drabold, *Phys. Rev. Lett.* **83**, 5042, 1999.
4. D. A. Drabold, X. Zhang and S. Nakhmanson in *Properties and applications of amorphous materials*, Ed. by M. F. Thorpe and L. Tichy, NATO ASI Series, Kluwer, Dordrecht (to be published, 2001).
5. A. A. Demkov, J. Ortega, O. F. Sankey, M. P. Grumbach, *Phys. Rev. B* **52**, 1618 (1995).
6. O. F. Sankey, A. A. Demkov, W. Windl, J. H. Fritsch, J. P. Lewis, and M. Fuentes-Cabrera, *Int. Journ. of Quant. Chem.* **69**, 327 (1998).
7. X. Zhang and D. A. Drabold, *J. Non. Cryst. Sol.* **241**,195,1998.
8. A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Dover, New York, 1996).