

Direct Calculation of Light-Induced Structural Change and Diffusive Motion in Glassy As_2Se_3

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Photostructural change of glassy As_2Se_3 was simulated on an experimentally credible model with excited electronic dynamics within first-principles molecular dynamics. Bond breaking and bond switching reactions account for local changes around defect sites at the short time phase of illumination. For long-time relaxation, defect pairs associated with band tail states become involved in a rearrangement in the network, giving rise to a low energy, nonlocal "polaronlike" collective oscillation. Diffusive motion is observed for short times, which we tentatively interpret as the initial phase of athermal photomelting.

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Under band-gap or subband-gap illumination chalcogenide glasses exhibit remarkable changes in physical properties. Depending upon the origin of changes, two types of light-induced metastable phenomena are observed. Following the classifications of Shimakawa and co-workers [1], one is the defect-related metastability, which is manifested by a change in electronic spin resonance, photoluminescence, and photoconductivity. The other is structure-related metastability, i.e., photostructural change, which includes photodarkening or photobleaching. In some systems global structure transformations, such as photoamorphization [2] or photoexpansion [3], are observed. Recent experiments have highlighted the importance of photostructural changes, which could develop into optomechanical devices for nanotechnology [4]. Tanaka has recently demonstrated a fascinating *athermal* photomelting in which weak, subgap light decreases the viscosity of $g\text{-As}_2\text{Se}_3$ by *several orders of magnitude*, and the effect is largest at low temperatures [5,6]. This effect is known only in glasses, and we report the first salient calculation here. These effects are spatially nonlocal, and as there are no realistic atomistic models available, limited progress has been made [7].

Earlier work on these problems has produced many simple and local candidates for structural components of the network believed to be susceptible to light-induced structural change. While most of these proposals are reasonable, they are not justified by any detailed calculations and are strictly *local*, though many light-induced effects are certainly nonlocal. This Letter is the first attempt in a binary chalcogenide glass to obtain a photostructural response by direct (albeit approximate) calculations on a realistic model, in this case the classic glass former As_2Se_3 .

It is believed that band tail states and their associated atomic groups in defect structures play a key role in photostructural changes, since these states are localized and therefore have a large electron-phonon coupling [8]. There have been no realistic calculations of defect and band tail states in glasses, however. It is here that a first-principles type molecular dynamics (MD) simulation can elucidate the nature of light-induced reactions. A simple and direct approach to light-induced effects has been proposed

by Fedders, Fu, and Drabold [9] for the Staebler-Wronski effect of $\alpha\text{-Si}$ and recently used by Zhang and Drabold [10] for $\alpha\text{-Se}$.

We constructed a 215 atom model of $g\text{-As}_2\text{Se}_3$ [11] using the program Fireball96 [12]. This turns out to be a realistic model featuring uniform agreement with three independent experiments on the structure [13], dynamics [14], and electronic properties [15]. A concise but revealing comparison between the model and experiments is given in Fig. 1. Our logic [16] is that if MD provides a model acceptably consistent with *all* the experiments we believe (both diffraction and spectroscopic), then the

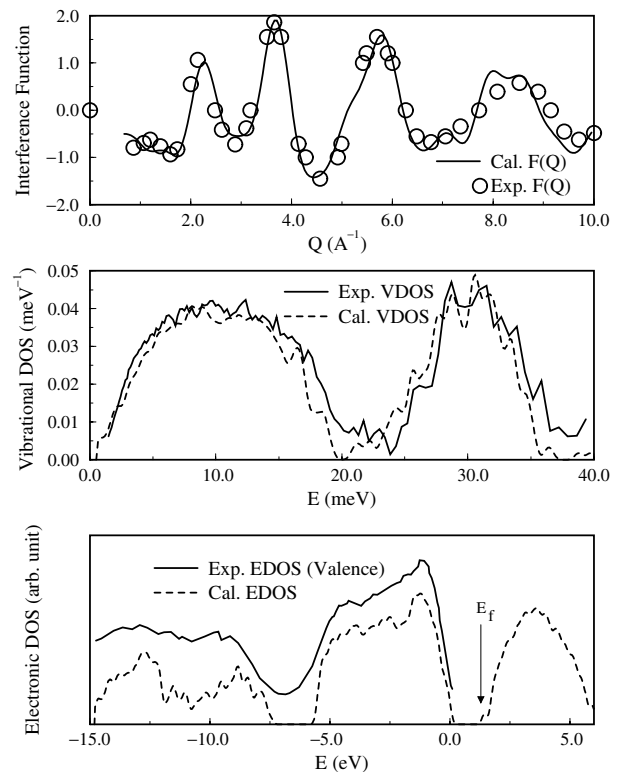


FIG. 1. A comparison between experiments and model. Top panel: the interference function $F(Q)$ [13]; middle panel: the vibrational density of states (VDOS) [14]; and lower panel: the electronic density of states (EDOS) [15].

model becomes worthy of additional study to investigate new phenomena, such as the atomistic origin of photostructural change in the glassy state.

Bonding defects in our model are as follows: three miscoordinated As: one twofold As (P_2) and two fourfold As (P_4), compared to 26 onefold Se (C_1) being paired with threefold Se (C_3) or P_4 : “valence alternation pairs” (VAPs, over-under coordinated pairs) [7]. Here, P stands for pnictogen atom As and C for chalcogen atom Se and the subscript indicates the coordination number. The edge states, i.e., highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are highly localized on coordination defect groups of As. The main defect structure of the HOMO group consists of an intimate VAP (IVAP, undercoordinated atom bonded to overcoordinated atom), P_2 - C_3 , and several subgroups from normal As and Se add a minor contribution around the main defect structure (shown in Fig. 2A). The main defect structure of the LUMO group consists of a random VAP (RVAP, where the atoms comprising the VAPs are separated), P_4 - C_1 , and a neighboring subgroup of C_3 (refer to Fig. 2B). The other P_4 in the present model has a structure similar to $(\text{Se}_{1/2})_3\text{As} = \text{Se}$ and is the dominant component of the state just above LUMO. Throughout the paper we define coordination using a radius of 2.8 Å, the first minimum in the equilibrium pair-correlation function.

Within the single-particle picture we model mild photoexcitation by boosting an electron from HOMO to LUMO. This produces an extra Hellmann-Feynman force [17] which puts the system into a nonequilibrium state [18]. The rationale for this is discussed in Ref. [10] and its cited references. We let the model freely evolve for 3 ps according to forces calculated from the excited electronic configuration without adding or taking away other energy, and track both the eigenvalues of band tail states and corresponding atomic motions during optical excitation. The first 1 ps evolution of the eigenvalues of band tail states and the average temperature is plotted in Fig. 3. After a rapid drop of the LUMO and slow increase of the HOMO, band tail states appear to arrive at an equilibrium. The final low temperature is consistent with a restoration of lattice-electron equilibrium.

We interpret the evolution on two time scales which emerge naturally from the simulation: short time (ST) stage and long time (LT) stage, as indicated in Fig. 3. The ST phase involves two atomic reactions. Bond breaking of homopolar bonds in the LUMO group occurs at the onset of illumination and accounts for the steep fall of the LUMO eigenvalue. The correlated coordination changes are found to be a bond transformation as indicated in Fig. 2. The antibonding character of the LUMO drives the weaker homopolar bonds to break and form energetically favored heteropolar bonds. This homopolar-heteropolar transformation may correspond to the experimentally observed “optical annealing” processes [1]. Associated with this rearrangement, energy is transferred efficiently from light

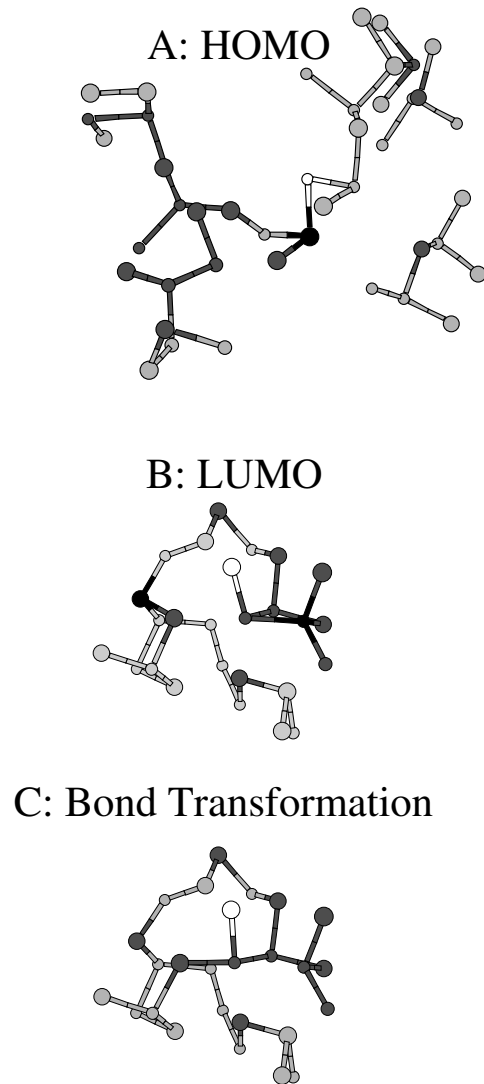


FIG. 2. A view of atomic groups at edge states. The small circle stands for As and the large circle for Se. Black (white) depicts over(under)-coordinated As or Se in main defect structure. Dark grey sites belong to minor contributors and light grey sites for others. All sites may have unshown bonds with other atoms. (A) HOMO's group; (B) LUMO group; (C) Homopolar-heteropolar bond transformation within LUMO group at the onset of illumination. Note: Two homopolar bonds, As-As and Se-Se, around over-coordinated sites in (B) break and a new As-Se bond has been created in (C).

(electrons) to lattice, yielding the rapid increase of temperature indicated in Fig. 3, while later reactions seem to be a low efficiency process for optical-vibrational energy transfer. The other reaction is a bond switch process occurring near the end of the ST stage and shown in Fig. 4A. This process indicates that light-induced unstable IVAPs are transformed into more stable RVAPs by bond switch processes. We found that bond switches are the main reaction in the relaxation of photoexcited states.

LT phase consists of a slow increase of the HOMO eigenvalue and concomitant atomic reactions (see Fig. 3). The long time scale emerges because the HOMO state is

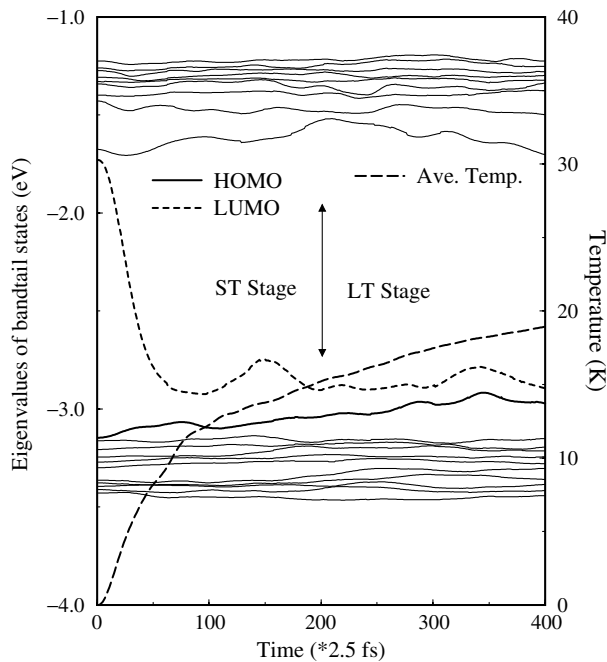


FIG. 3. The first 1 ps evolution of eigenvalues of band tail states and average temperature simulated for model of $g\text{-As}_2\text{Se}_3$ under illumination.

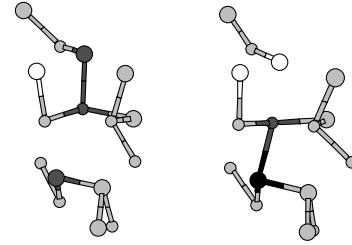
less localized than the LUMO. Photomobile atoms are from satellite minor contributors of HOMO. Bond switch processes in the LT phase are different from those at the ST phase. An event is depicted in Fig. 4B. At the LT stage, (R)VAPs have been rearranged along with atomic groups of edge states. It is worth pointing out that the rearrangement of (R)VAPs is coupled with the nonlocal vibration of the network, which is driven by reactions at the ST stage.

We have noted that the energy transfer from electron to lattice in the ST phase is essential to enable bond switching in the LT phase. This indicates that the regular bond switches at the LT scale is a collective effect due to light and lattice motion upon the atomic groups of edge states.

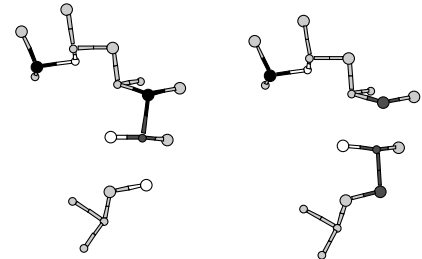
Bond switch processes seem to cease after the LT phase and a regular nonlocal collective oscillation has been observed for later times. In other words, a balance between network dynamics and photoexcitation develops after about 1.4 ps illumination. This nonlocal collective motion involves an oscillation around the atomic groups of edge states and spans a long intermediate range (almost half of the atoms in our model are involved). Figure 4C depicts a section of highly oscillating regions featuring a periodic relative motion between atoms in the network. From the observed period (>200 fs) this “polaron” like motion has an estimated energy of no more than 20 meV corresponding to extending modes in the low frequency phonon region. However, the final average temperature develops only to about 25 K (~ 2.16 meV).

When we “turned off the light” (returned to the electronic ground state) and quenched, a fourfold As was cre-

A: Bond switch at ST stage



B: Bond switch at LT stage



C: "Polaron" mode

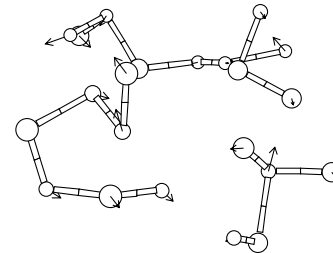


FIG. 4. Two types of bond switch processes viewed from left to right. (A) The ST stage: An IVAP was created by breaking an As-Se bond and transferred to a RVAP subsequently as the new P_2 went to combine with a nearby C_2 , which was converted into a C_3 defect. Involved atoms are the subgroup of LUMO's structure in the right side part of Fig. 2C; (B) the LT stage: A bond around C_3 broke to create a P_2 defect and subsequently the new P_2 defect combined with a nearby C_1 defect. A RVAP was eliminated. Atoms are those at the corner of the upper right of Fig. 2A. (C) Schematic of oscillating regions of the “polaron” in the network. The arrow indicates the atomic motion with magnitude proportional to displacement.

ated in the “polaron” volume and eigenvalues of band tail states tended to recover. But some bond switch effects were frozen in, which reduced the number of homopolar (wrong) bonds and miscoordinated sites. Thus as a by-product of illumination the whole structure was improved, an “optical annealing” process as observed in experiments. This annealing occurs in part because the network is attacked (and annealed) rather surgically, exactly in the region of the defect. However, it is very interesting that a nonlocal collective oscillation in intermediate ranges is finally established from only local reactions.

We have also investigated promotion to levels above the LUMO. The promoted electron quickly mixes with nearby levels, and rapid oscillations in bond length are observed near the weak bonds that broke for direct promotion to

LUMO. For this case, adiabatic dynamics may fail—we are currently exploring this [17].

We computed $\langle r^2(t) \rangle$, the system-average mean-squared variation in atomic position from the initial conformation. After 50 fs the curve is very linear until beyond 1 ps. We interpret this as a diffusive regime (a *light-induced* self-diffusion constant of $D = 1.16 \times 10^{-5} \text{ cm}^2/\text{s}$ is obtained), because its feature is consistent with diffusion observed in l-GeSe₂ approaching the melting point [19]. This is the first tentative calculation of the short-time character of athermal photomelting [5]. Beyond 1 ps $\langle r^2(t) \rangle$ flattens. Presumably somewhat stronger photoexcitation or some assistance from thermal phonons would be sufficient to explain the viscosity changes reported by Hisakuni and Tanaka [5]. *Even starting at $T = 0 \text{ K}$ and promoting one (of 1204) active electrons leads to diffusion over 1 ps.* In the crystal under similar conditions, no bond breaking or diffusion is observed. We note that our observation is certainly not a complete explanation of the photoinduced fluidity, but we think that the occupation of low lying conduction states gives already weakly bonded atoms additional freedom to diffuse in the network and in the extreme condition leads to photomelting, while the conventional thermal diffusion or melting depends on the lattice dynamics of atoms.

In conclusion, atomic dynamics has been proposed for photostructural changes in *g*-As₂Se₃ based on first-principles MD simulation. The homopolar-to-heteropolar bond transformation is observed around overcoordinated sites at the onset of illumination. Two types of bond switch reactions are observed. One involves the generation of VAPs at the short time stage. The other one makes VAPs redistribute in the LT scale and establish a final nonlocal “polaron”-like collective oscillation in space. Atomic groups around defects play a key role in the LT scale, which couple the local effects of bond switch reactions with the nonlocal low energy vibration in the network. Defect structures from different edge states have shown an opposite tendency under the influence of light. It suggests that extra electrons in antibonding levels tend to create VAPs while holes in lone pairs tend to serve as a recombination center to eliminate VAPs. Bond switch processes could be a candidate channel of photoconductivity [1]. There maybe are some finite-size effects even in

this 215 atom model. However, there appear to be only so few basic types of reactions in the present simulation, it is reasonable to believe that this simulation provides insight into these light-induced effects. Finally, we emphasize the *nonlocality* of the entire process and the need for atomistic simulation to study photostructural effects.

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