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Electronic consequences of the mutual presence of thermal and structural disorder

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We investigate the simultaneous presence of topological and thermal disorder in amorphous silicon. We find that localized electronic states are *very* sensitive to moderate amounts of thermal disorder: for a given gap or band tail electronic eigenstate, both the fraction of the total charge on a given site as well as the energy eigenvalue can vary greatly with small (thermally accessible) changes to the positions of the atoms. This observation, which is almost certainly relevant to any disordered insulator including glasses, has important implications to the microscopic theory of transport, optical properties, and doping, as well as existing models of defect kinetics. [S0163-1829(99)50426-8]

Amorphous semiconductors and glasses are important materials employed in a wide variety of electronic and opto-electronic applications. All such applications depend critically on the nature of the electron states near the Fermi level (since conduction, for example, depends on transitions near the Fermi energy). In summary, we will show that modest amounts of thermal disorder, superposed onto a structurally disordered network, are sufficient to dramatically change the energy and structure of band tail electronic eigenstates on time scales of order 50 fs (a time characteristic of lattice vibrations). These fluctuations in structure of the eigenstates occur *only* if there are localized energy states adjacent both within energy (meaning within a few tenths of an eV), and real space, and such that the thermal disorder at a given temperature is sufficient to occasionally bring the energy eigenvalues of the adjacent states very close together. These conditions are often met in realistic models of *a*-Si for states near the Fermi level at room temperature. In applications, one is usually interested in doped semiconductors, where the Fermi level is shifted away from the middle of the optical gap into either the conduction or valence band tails. Thus, the picture that emerges is one where the energy eigenvalues and sites where those eigenstates are localized change rapidly and drastically in a quasioscillatory (but not periodic) manner. Further, the sites where a state is most localized may form wandering stringlike structures or columns where no

two favored sites are nearest neighbors. However, in a variety of physically relevant temperature and energy ranges states, they never form a static structure, and often a spherical approximation for their geometry would be inappropriate. This is very different from the prevailing view. While we have limited the current study to *a*-Si, there is every reason to believe that the qualitative picture we present here is suited to any disordered insulator, such as glasses.[1] Unfortunately it is very difficult to directly connect these results to experiments because the time scales are very short; yet the ideas contained here are important in constructing proper theories of transport and optical effects.

This work overlaps an important body of existing theory work. Phenomenological theories of defect dynamics and kinetics (the defect pool model[2]) and transport[3] have solved outstanding problems in their respective areas in *a*-Si and glasses. A value of the present work is to elucidate the foundations of these approaches by describing *explicitly* the nature of the electron states and their short-time dynamics. This will hopefully enhance and extend the value of these theories, and perhaps enable *ab initio* input to the phenomenological models. An important complement to this paper is the existing work on temperature dependence of electronic energies in crystals, presented by other authors.[4] In this paper we employ the approximate local basis *ab initio* molecular-dynamics scheme of Sankey and co-workers.[5] The method is tested for Si in many forms and is quite reliable. As in pre-
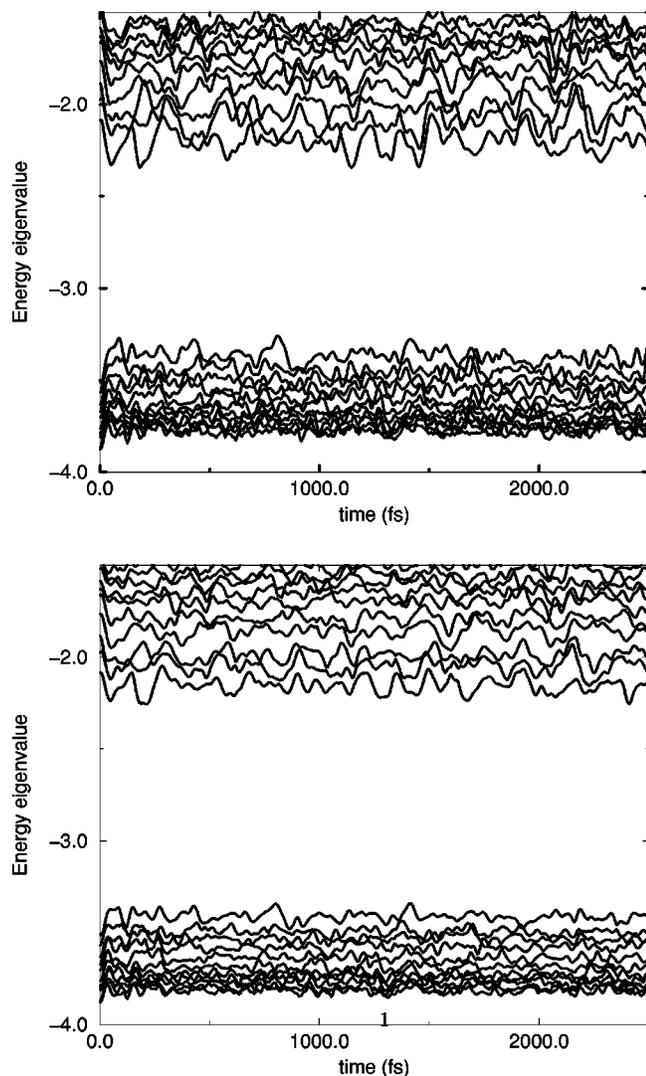
FIG. 1. Approximate LDA energy eigenvalues plotted against time (in fs) for a 216 atom model (Ref. 6) from 300 K thermal simulation. The Fermi level is in the middle of the optical gap (near -2.7 eV). Note the large thermal fluctuations in the eigenvalues near the gap, and the occasional close approach of neighboring energy eigenvalues. The top panel is for a simulation at 300 K; the lower panel for 150 K (see text).
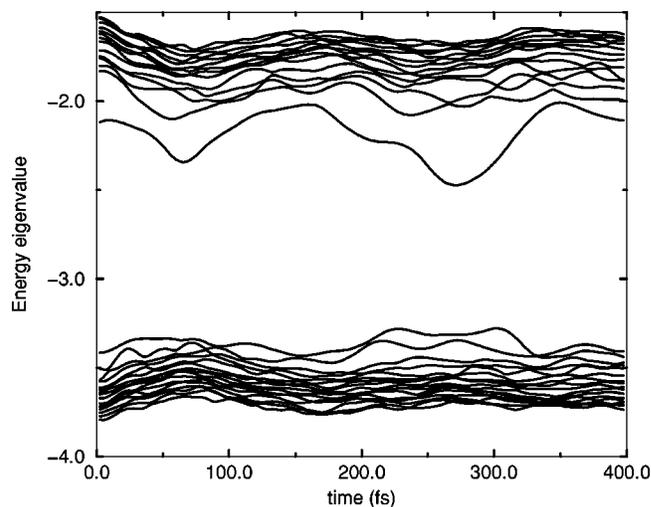

FIG. 3. Approximate LDA energy eigenvalues plotted against time (in fs) for a 512 atom model (Ref. 6) for 300 K thermal simulation. The Fermi level is contained in the gap (near -3.0 eV).

vious work, we start with relaxed versions of the supercell structural models of Djordjevic, Thorpe, and Wooten,[6] which are currently the most realistic models of a-Si extant since they are the only ones to our knowledge which *simultaneously* reproduce structural, electronic/optical,[7] and vibrational properties of a-Si. We describe this elsewhere.[8]

We briefly discuss three approximations utilized in this work relevant to the electronic states and the influence of thermal disorder on them. (1) *The Born-Oppenheimer approximation*.[9] We assume here electrons follow the nuclear motion adiabatically, so that the electron state deforms progressively by nuclear displacements. The details of an electronic transition cannot be obtained from an adiabatic simulation. Yet the main features (large modulation of eigenvalues and large variation of conjugate vectors) are surely properly reproduced with such an approach. In addition, the atomic motion is classical; the nuclei move in a classical potential derived from the electronic structure. At lower tem-

peratures a phonon picture would be necessary. (2) *Literal interpretation of Kohn-Sham eigenvalues*. There is no rigorous basis to this assumption. We rely here on the experience of a number of researchers which shows that useful information may be extracted from the eigenvalues and vectors of density-functional theory (even for transport).[10,11] (3) *Finite-size artifacts* are certainly relevant for any study of localized states using periodic boundary conditions, which is partly why we have adopted a Hamiltonian capable of describing the dynamics of as many as 512 atom cells.

In Fig. 1 we indicate the time dependence of the local-density approximation (LDA) eigenvalues in the vicinity of the optical gap. The Fermi level is near the middle of the gap and several states near the Fermi level are appropriately described as band tail states. These are much like the states which would be responsible for conduction in doped a-Si:H. The top panel illustrates the effect for a simulation at 300 K, the bottom panel for 150 K. As in earlier work[12] there is a roughly linear relation between rms temporal fluctuation and temperature. As expected, the higher temperature simulation leads to larger excursions in the positions of the energy eigenvalues. Note for Fig. 1(a) (300 K) that the lowest unoccupied molecular orbital (LUMO) fluctuates in time by ~ 0.3 eV, *much* larger than thermal energies (~ 10 meV). States deeper into either the valence or conduction bands show progressively less thermal modulation because they are less localized (we have noted[1] a very strong correlation between the rms fluctuation in the energy eigenvalues due to thermal disorder and the inverse participation ratio, a simple measure of localization in the $T=0$ model). The localization ''amplifies'' the electron-phonon coupling. Also, the conduction states fluctuate more than the valence states (suggesting that the conduction tails are more sensitive to thermal disorder than the valence tails which originate primarily from structural disorder), in pleasing agreement with total yield photoemission experiments[13] and earlier theory work.[12]

The key conclusions of this paper can be inferred from Fig. 2, in which we illustrate ''snapshots'' of a particular electronic eigenvector (the LUMO state) extracted from a 300 K simulation of a-Si.[14] In these figures, different colors
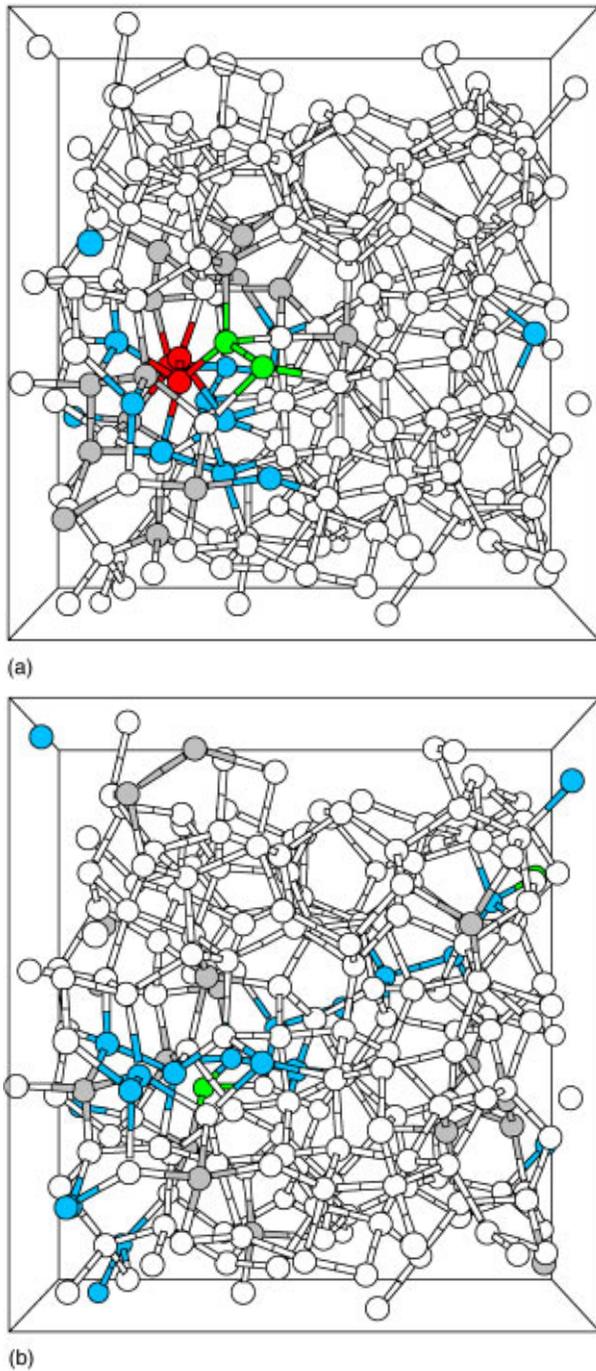
(a)

(b)

FIG. 2. (Color) A representation of the LUMO energy eigen-state and the time dependence of its structure, as modulated by thermal disorder for a 216 atom model (Ref. 6) from 300 K simu-lation. The color coding reflects different amounts of electron charge on a site: Red ($q>0.1$), green ($0.05<q<0.1$), blue ($0.05<q<0.01$), grey ($0.01<q<0.005$), and white ($q<0.005$). q is the total charge on the site. The charge summed over all sites is unity in all cases. (a) and (b) are ''snapshots'' from the 2.5 ps simulation. (a) is a very localized compact cluster, (b) a ''string''-like state, much less localized than (a). These are only ''snapshots'' and de-pict only the two most commonly recurring structures of the LUMO state.

indicate different levels of charge on a given atom (the or-dering is red, green, blue, gray, white; see the caption for detail). There is a clear tendency for the LUMO state to alternately ''accumulate'' on a strained part of the network,
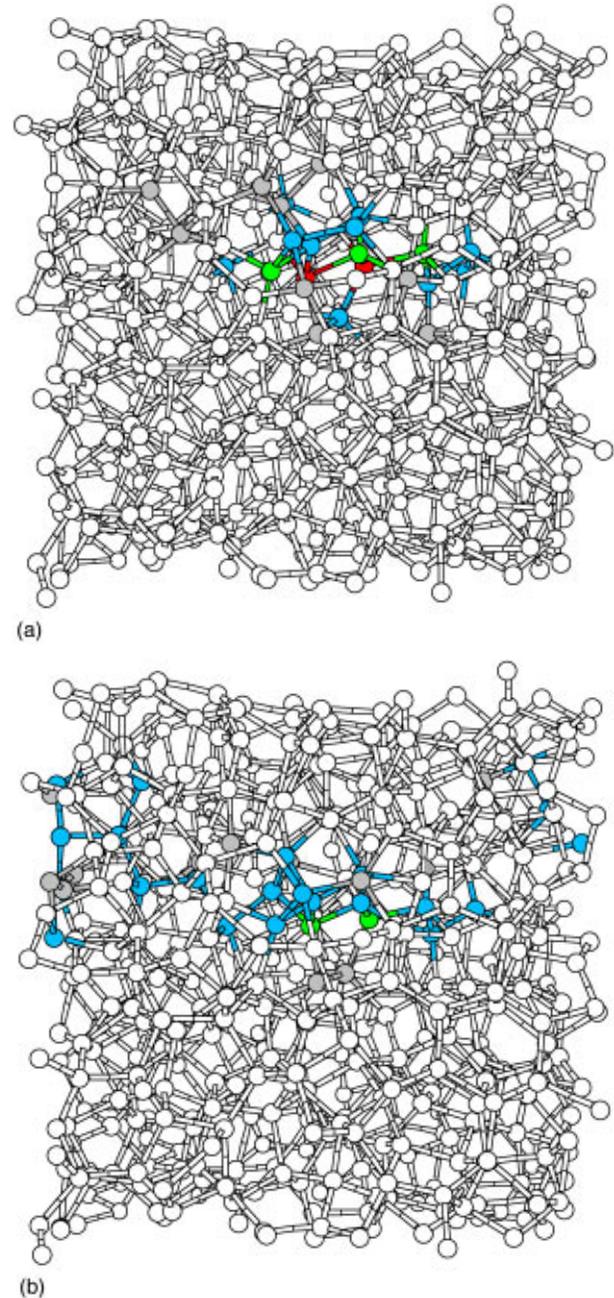
(a)

(b)

FIG. 4. (Color) A representation of the HOMO energy eigen-state and the time dependence of its structure, as modulated by thermal disorder for a 512 atom model (Ref. 6) from 300 K simu-lation. Same color mapping as Fig. 2.

sometimes becoming strongly localized [Fig. 2(a)], but also occasionally developing a substantially more extended ''stringlike'' character [Fig. 2(b)]. These are not the only two recognizable structures, but recur most frequently. The time between ''characters'' is not predictable, though it is of order tens of hundreds of fs.

In Fig. 3, we reproduce the 300 K temporal fluctuations of the LDA eigenvalues near the gap for a larger (512 atom) model of a-Si also made by Djordjevic et $al.$,[6] and also in excellent uniform agreement with experiments. This larger model illustrates some additional points. Although the LUMO energy level fluctuates considerably, the structure of its conjugate eigenvector is much more ''static'' than the

LUMO state of Fig. 2. Even though there is obviously a large electron-phonon coupling (because of the large fluctuations in energy), the state does not approach closely enough to the next conduction state in energy to exhibit strong mixing and therefore markedly change its structure. This emphasizes the point that a large electron-phonon coupling *by itself* is not sufficient to cause major changes in the structure of the relevant eigenvector. In Fig. 4, we illustrate the highest occupied molecular-orbital ''HOMO'' state and snapshots in analogy with Fig. 2. By inspection of the time development of this state from Fig. 3, there are two ''close approaches'' of this state to the next valence tail state. Indeed we find that the qualitative behavior of this state is similar to that from Fig. 2; ''snapshots'' with identical color coding to Fig. 2 are presented as Figs. 4(a) and 4(b), illustrating compact cluster and chainlike character, respectively. In the short simulation for the 512 atom model (400 fs), we also saw a distinctive structure involving three rather separated clusters. We conclude that the phenomenon is qualitatively similar for occupied levels such as this or for unoccupied states (the LUMO of Fig. 2).

We have argued earlier[15] that structural disorder in a-Si gives rise to localized states with energies in the band tails. These system eigenstates can involve *many* atoms and can have a Byzantine structure. This work[15] showed that it is useful to view localized energy eigenstates in a-Si as either pure or mixed ''cluster states.'' Cluster states are localized eigenstates of an idealized system which stem from some structural irregularity such that there is no overlap with energetically degenerate clusters. Such cluster states can be difficult to realize *in isolation* in *real a*-Si, since structural defects can occur with similar local electron energies, which would cause the system energy eigenvectors to consist of mixtures of the resonant defect clusters if the defects are in adequate spatial proximity to allow overlap between cluster states. We have explained this in Ref. 15. The ''simple physics'' of this paper is that the strong electron-phonon coupling for localized band tail states *is sufficient* to cause strongly time/temperature dependent quantum mechanical mixing of cluster states when the thermal disorder is ''just right'' to make their energies nearly degenerate provided that they have some overlap in real space. Strong mixing of course implies less localization and thus better prospects, at least while the more extended state survives, for conductivity and optical transitions. This work shows that transport and optical calculations based only on $T=0$ results can be quite mis-leading. Mott[16] and others have made fundamental contributions to the theory of transport in a noncrystalline medium; for example, variable range hopping. In the kind of simulation we present here, one can estimate the conductivity, including its temperature and frequency dependence, *directly* from the electronic states through an appropriate thermal average of the Kubo[17] formula. It is also a complement to the phenomenological models of transport.[3] In the latter work, transport is modeled as a hopping between localized tail states. Our work can be viewed as an explanation of the precise nature of the states among which electrons are hopping (the very complicated states of Figs. 2 and 4, and Ref. 15). The waiting time between hops must be related to the time between eigenvalue ''close encounters'' or level crossings near the Fermi level. It also points at an atomistic level to the dynamics of bandtail defects and their kinetics.

The consequences of this work can be stated another way. If $|i\rangle(|f\rangle)$ are initial (final) electronic states with energy $E_i(E_f)$, then for an electronic transition in a-Si, a Fermi golden rule argument leads quicky to the conclusion[16] that the transition rate is proportional to $|\langle i|\hat{T}|f\rangle|^2\delta(E_f-E_i-\hbar\omega)$, where $\hat{T}$ is a perturbation inducing the transition (to first approximation a momentum operator) and ω is the frequency of an external probe. Both the energies in the δ function and the transition matrix elements are sensitive to the instantaneous details of the structural disorder, and as such transition probabilities are also strongly dependent on the time and temperature. The consequences of this to transport are under investigation; the discussion here is based upon first-order time dependent perturbation theory, which for the very strong electron-phonon coupling we discuss, could be inadequate.

In conclusion we have found a strong time dependence in the energy eigenvalues and states near the Fermi level in a-Si at ordinary temperatures. We expect the phenomenon to be much more general; certainly occurring in glasses, but probably in insulating liquids and perhaps polymers as well. The origin of the effect is a strong electron-phonon coupling for the localized band tail states plus a reservoir of energetically adjacent states with which quantum mixing can occur, as driven by the lattice vibrations.

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