Long-range structural and electronic coherence in amorphous semiconductors

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We use curved-space polytope lattices to model the defect-free regions of amorphous semiconductors. A particular structural feature, a channeling axis associated with a local screw symmetry, is suggested by the polytope model and can be found in previous amorphous network models. Its presence implies electronic eigenstates with phase coherence over many bond lengths. We present a "band structure" for amorphous Si based on this coherence.

Structural experiments[1] indicate that tetrahedrally bonded amorphous semiconductors preserve a high degree of short-range order (SRO). Other experiments[2] which probe the nature of band edge eigenstates in amorphous silicon (a-Si) provide evidence that this structural SRO manifests itself in a phase coherence reminiscent of Bloch phase coherence in crystals. Analysis of optical and transport data[3] shows that models which assume completely random phases cannot account for both the form of the band tails and the width of the exponential absorption tail in hydrogenated a-Si. In this paper we consider SRO and its effect on the eigenstates of a-Si. We use a-Si generically to denote a-Si with or without hydrogenation.

At a minimum, SRO means the preservation of fourfold coordination in the amorphous solid. We refer to this as "weak" or "fourfold SRO." These materials actually preserve a stronger form of SRO in which chemical bond lengths and, to a lesser extent, regular tetrahedral bond angles are preserved; we denote this as "strong" or "tetrahedral SRO." Cluster models incorporate the tetrahedral SRO by accurately representing the structural relationships among small groups of atoms (~ 5–8), while approximating the remainder of the amorphous network with a judiciously chosen set of boundary conditions. Commonly used boundary conditions include H termination,[4] artificial periodicity,[5] etc. Cluster models have been useful in elucidating the connections between specific small structures in the lattice (e.g., rings of bonds) and features in the electronic structure. We also classify the cluster Bethe lattice technique[6] among the cluster models. By the nature of their construction neither the Bethe lattice nor the cluster models can address the possibility of structural coherence among larger groups of atoms, which is the feature we study in this paper. Another class of models, the network type,[7] produces large-scale structures (several hundred atoms) constructed to obey the requirements of "fourfold SRO." For the first few neighbors these models give a good representation of actual amorphous radial distribution functions. Therefore, network models have been used extensively in the study of electronic and vibrational states of amorphous materials.[8] Network models can represent averaged structural properties, but do not provide a starting point for an investigation of long-range structural coherence. First, they assume that strains and other deviations from "tetrahedral SRO" are homogeneously distributed throughout the lattice. Small angle scattering[9] demonstrates that strain is not uniformly distributed, but is more likely to be concentrated in defect regions. We infer that the intervening network obeys the rules of strong SRO almost rigidly, particularly for hydrogenated a-Si.[10] Second, the network models are not built with the intention of incorporating long-range structural coherence in any systematic way, and structural correlations at large separations are not considered. There is increasing evidence that such long-range correlations exist in disordered systems,[11] and we will show later that they probably exist in the network models as well.

There is a new, third class of structural models for amorphous semiconductors.[12] These are called "polytopes" and are uniquely suited as models of possible long-range structural correlations. Polytopes,[13] regular tilings of positively curved three-dimensional (3D) space, have recently proven useful in the study of metallic glasses and cholesteric liquid crystals.[14] Several of the polytopes are reasonable structural models insofar as they contain only fourfold coordinated lattice points and have reasonable ring sizes (5 and 6). The curvature of the space permits the polytopes to have *perfect* "tetrahedral SRO" and complete long-range order as well. This ideal order is representative of approximate long-range structural coherence in the real amorphous solid; we demonstrate an explicit example for a-Si below. We also describe the symmetries associated with this long-range order. From these we uncover a family of symmetry quantum numbers which may be used to label the phase coherence of eigenstates resulting from long-range structural coherence. We show such a classification of electronic eigenstates for a-Si below, and demonstrate the strong analogy to the

momentum labeling "k" for eigenstates in crystals. Of course, no model in curved space can provide a complete representation of the actual flat space amorphous network. However, the curvature of the polytope space is fairly small and up to about 100 lattice points of the polytope can be mapped into flat space with only small distortions.[12] This suggests that we might expect long-range structural coherence in amorphous solids in clusters of about 100 atoms; a previous model of the electronic properties of a-Si has assumed such clusters with some residual order.[15] Also, since the polytopes have perfect order, well characterized defects (e.g., disclinations) can be introduced,[12,14] which may provide the starting point for a model for the interface between neighboring clusters each with some internal order.

We turn now to a specific polytope that is representative of an actual tetrahedrally bonded solid. We choose the 240 atom polytope generated by the decoration of (3,3,5), the regular packing of tetrahedra in curved three-dimensional space,[13] which bears the same relation to (3,3,5) as the diamond lattice bears to the fcc crystal structure. Polytope 240 contains several features which make it desirable as a model of a-Si. First, it has a reasonable atomic density, comparable to that of crystal Si and of the highest quality a-Si. Second, it contains all sixfold rings; the more successful network type models contain a large number of sixfold rings.[7] The shape of these rings is a distortion of the classic "boat" type. Consequently, clusters from polytope 240, when examined in Euclidean space, have a rather "disordered" appearance. It has not been previously pointed out that despite this apparent "disorder," the lattice contains a high degree of long-range order. Around one axis polytope 240 has a threefold symmetry rotation and a sixfold screw axis,[16] i.e., $(R_{xy},R_{zt})=(2\pi/6,2\pi/6)$, around another axis there is a tenfold screw axis $((R_{xy},R_{zt})=(2\pi/10,2\pi/10))$. Around a third axis, polytope 240 has another symmetry which is of particular interest to us: a unique compound rotation $(R_{xy},R_{zt})=(2\pi/30,2\pi\times\frac{11}{30})$. Figure 1 shows the configuration of the Si atoms around the core region of the 30/11 axis. This axis passes through the center of a series of sixfold rings which form an open path through the polytope similar to a channeling direction in a semiconductor crystal. This path may also be described as a triplet of (110)-like chains of atoms which are bonded together and twisted around each other. One of these chains has been dashed in Fig. 1. Model construction demonstrates that the local strains are low, suggesting that this configuration is locally a low-energy state of the a-Si lattice. The possibility of channeling paths in a-Si is implicit in previous work,[17] and these open paths can be discerned across the entire width of handbuilt network models of several hundred atoms.[18] While we could have focused our attention on the sixfold or tenfold axes mentioned above, the 30/11 axis is a better candidate for local order in a-Si since it actually occurs with reasonable frequency in real structures. Polytope 240 thus demonstrates its usefulness in enabling us to pick out and identify a specific large-scale structure in the amorphous network. In fact, the polytope tells us much more. Since the channeling axis is associated with a specific 30/11 screw symmetry, the electronic or vibrational eigenstates in the vicinity of this axis, far from being random, maintain a very specific long-range phase relation [similar to that illustrated for a curved polymerlike chain in Ref. 10(b), Fig. 1] which is labeled by the representations of the 30/11 symmetry group. These labels are of the very simple angular momentum type.

To demonstrate explicitly the organization which the 30/11 symmetry imposes on the eigenstates, we have computed the electronic structure of the polytope using a Si tight-binding Hamiltonian.[19] If the channeling path were infinitely long, the angular momentum quantum number would become a continuous variable analogous to a crystal momentum k, and the eigenstates could be displayed in a one-dimensional band diagram. This is the scheme used in Fig. 2. This figure possesses many of the familiar features of the electronic band structure of Si, including the ~ 1 eV band gap, the ~ 12 eV wide valence band, and as shown previously,[10] the three-peaked valence band density of states. The channeling axis on which these energy bands are based is not infinite; in the ideal polytope lattice it closes on itself after 30 twists. These boundary conditions pick out 30 "allowed" k values, shown as the points on Fig. 2.

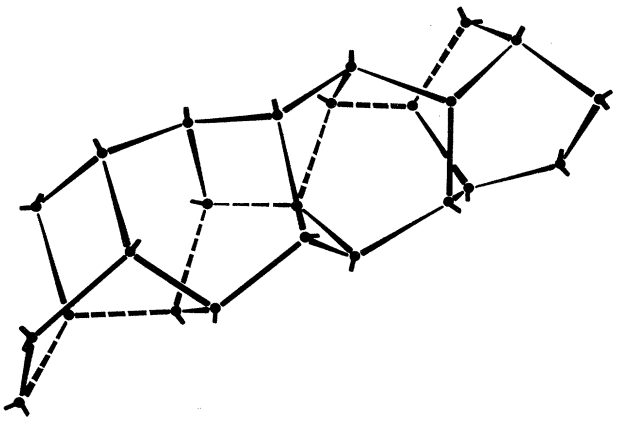

FIG. 1. The local bonding arrangement of Si atoms around the 30/11 channeling axis. One of the (110) chains is shown dashed.

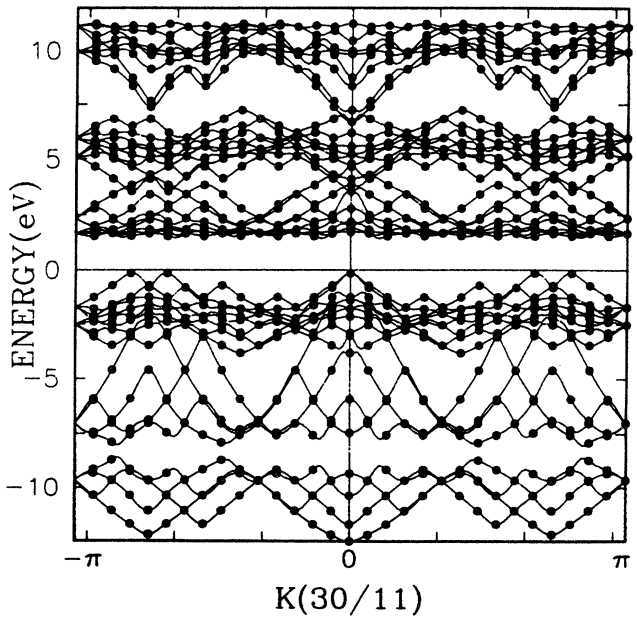

FIG. 2. The energy band structure of polytope 240. The solid points show eigenvalues at the "allowed" k values of the polytope.

These are the actual eigenvalues of polytope 240. We expect that in the real amorphous network the typical channeling axis will terminate after a comparable distance, generating a similar set of allowed k values. The general appearance of Fig. 2 is similar to that of a surface band structure with finite areas of allowed states surrounding energy gaps in certain regions of the Brillouin zone. This is not surprising, since as mentioned above, the channeling axis onto which the energy bands are projected may be viewed as a (110) internal surface (folded so as to have perfect fourfold coordination). To be specific, we predict that the energy bands in Fig. 2 should be closely related to the (110) surface energy bands along the $(3\bar{3}1)$ direction in reciprocal space. The real significance of Fig. 2 is the fact that it can be drawn at all. By identifying a quantum number k which can label the electronic eigenstates and which has a physical basis in the local structure of a-Si, we immediately impose symmetries on any processes involving the eigenstates (e.g., vertical selection rules in optical absorption[10]).

It was previously shown[10] that the polytopes share with the cluster type and network type models the ability to predict some general properties (e.g., the density of states) of the amorphous state. We have now shown the ability of the polytope model to suggest and identify long-range coherence (e.g., channeling structures) in apparently random networks. The existence of such large scale structural coherence implies a long-range phase correlation of the amorphous eigenstates. These phase correlations are classified according to the symmetry group of the polytope; this classification is analogous to k in a crystal and allows us to organize the energy eigenvalues into an energy band diagram. The suggestion of phase correlations in the amorphous state calls into question the central assumption of many interpretations of optical and transport data. For example, we have recently shown[10(a)] that the 30/11 symmetry can have important matrix element effects on $\epsilon_2(\omega)$ near the band threshold in a-Si. Some experiments (e.g., the pressure dependence of the optical absorption[2]) have already suggested the possibility of a remnant of some crystal-like phase coherence in a-Si; other experiments should be possible to probe additional aspects of long-range order in amorphous semiconductors.

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