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Density of states in crystalline and amorphous germanium*

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The density of states in crystalline and amorphous germanium are obtained directly from 47-atom-cluster calculations using the extended Hückel theory (EHT), with the specific intention of comparing the changes in their characteristics as Ge takes on these forms. Diamond lattice is assumed in the crystalline cluster. The Henderson-Herman and the Polk-Boudreaux model coordinates are used in amorphous Ge. Observed changes in the density of states are discussed and compared with previous studies. EHT proves to be a simple and practical method in the study of disordered systems.

The purpose of this study is to obtain fairly good estimates of the density of states in crystalline and amorphous germanium with the specific intention of comparing the differences in their characteristics. They are calculated on the same theoretical basis by the same computer program to the same accuracy.

The most serious problem in the theoretical study of the electronic properties of amorphous Ge is the structural disorder. Lack of periodicity renders the $\vec{k}$-space formalism less meaningful. The more direct approach is the cluster calculations in $\vec{r}$ space. The cluster multiple-scattering approach using spherical muffin-tin potentials fails to represent the directional properties of the covalent bonds in Ge.[1] A full multiple-scattering calculation, even for small clusters, is extremely laborious.[2] Studies on the averaged properties of various crystalline polymorphs[3] give much valuable information, but such an approach is indirect. Tight-binding calculation studies the lower portion of the valence band.[4] All these factors—cluster approach, covalent bonding, and practical computational simplicity (retaining to some extent the nature of an *a priori* calculation)—led us to turn to the methods that were developed by chemists specifically for covalent hydrocarbons, and which are well tested on molecular clusters. The method used here is the extended Hückel theory (EHT).[5]

The success of EHT applied to nonpolar hydrocarbons in predicting configurations and molecular-orbital energies is well known.[6] Recently, it has been used to calculate crystalline band structures,[7] and the results, especially for diamond,[8] are amazingly good. EHT calculates the energy eigenvalues and eigenfunctions of all the cluster "molecular" orbitals with very minimal input information: the atoms involved and their coordinates. It is therefore very suitable for our purpose. In fact, calculating an amorphous cluster is just as easy and as accurate as calculating a crystalline cluster. Computation is fast—about 6 min for a cluster of 47 atoms using a CDC 6400. As expected, the matrices for large clusters take up most of the computer core space, and this is the major restriction in our present report.

The Ge atom is characterized by two orbital ionization potentials[9] and two exponents in the Slater-type atomic orbitals[10] for the *s* and *p* states. We have not included the *d* orbitals to save core space. There remains the one adjustable parameter K, in EHT chosen to be 1.75 following the original suggestion of Hoffman.[5]

The basis of cluster calculation is the belief that the properties of disordered systems are mainly associated with the characteristics of the constituent atoms[11] and their local surroundings.[2,12] The radial-distribution function of amorphous Ge differs from that of the liquid mainly in the absent, or very small, third-neighbor peak.[13,14] It is desirable to have large enough clusters to go beyond this third peak. In the diamond lattice, there are 29, 35, and 47 atoms lying inside the third-, fourth-, and fifth-nearest-neighboring shells, respectively. The maximum number of scatters studied previously is 30.[2] All our clusters have 47 atoms (computer core-size limitation).

The crystalline cluster is chosen to be the first five nearest neighbors in the diamond lattice. This cluster encloses all the third neighbors but is not large enough to have all the third-neighbor bonds joined to a Ge atom. Both the Henderson-Herman (HH)[15] and the Polk-Boudreaux (PB)[16] models for amorphous Ge are studied. In the 61-atom periodic HH model, an atom near the center of a unit cell is chosen. This atom and its nearest 46 neighbors form a sample set of 47 atoms in our calculation. The PB model (519 atoms) is large enough so that

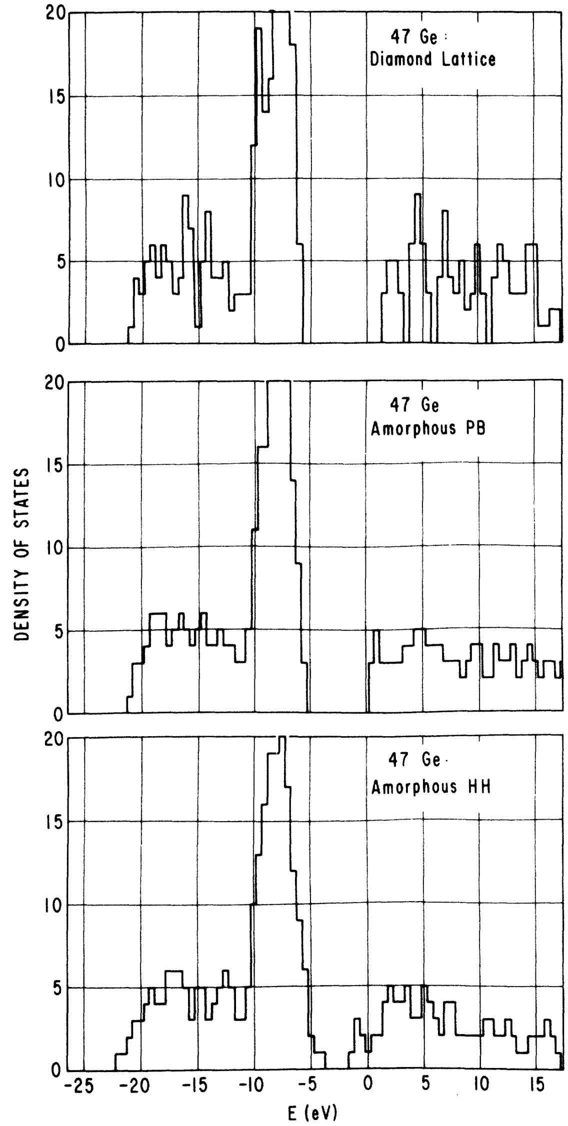

FIG. 1. Density of states of (a) crystalline (diamond) structure, (b) amorphous (Polk-Boudreaux) model, and (c) amorphous (Henderson-Herman) model, in 47-atom clusters.

our 47-atom clusters can be taken from the central portion without including the "surface" atoms of the original PB cluster. The 47-atom clusters are isolated in a vacuum. This is the most convenient and also the most studied boundary condition in EHT calculations. We do know a lot about the surface states in isolated diamond clusters.[8] Relatively little is known about the periodic boundary effect on amorphous clusters. We emphasize our intention is to look for the differences in the density of states in the crystalline and in the two-model amorphous Ge clusters. We believe the surface conditions in the three clusters are similar enough so as to contribute in about the same way. The results are shown in Fig. 1, and the three histograms must be considered as a group. Absolute features are less reliable because of the noise and surface states.

Comparing the density of states obtained from a full-band-structure calculation of crystalline Ge[17] with our cluster calculation [Fig. 1(a)], we see that all salient features are present. There are two peaks in the lower part of the valence band (see discussion below in relation to Fig. 2), a major peak near the top of the valence band with a small branch on the low-energy side, and a relatively smooth conduction band. The valence-band

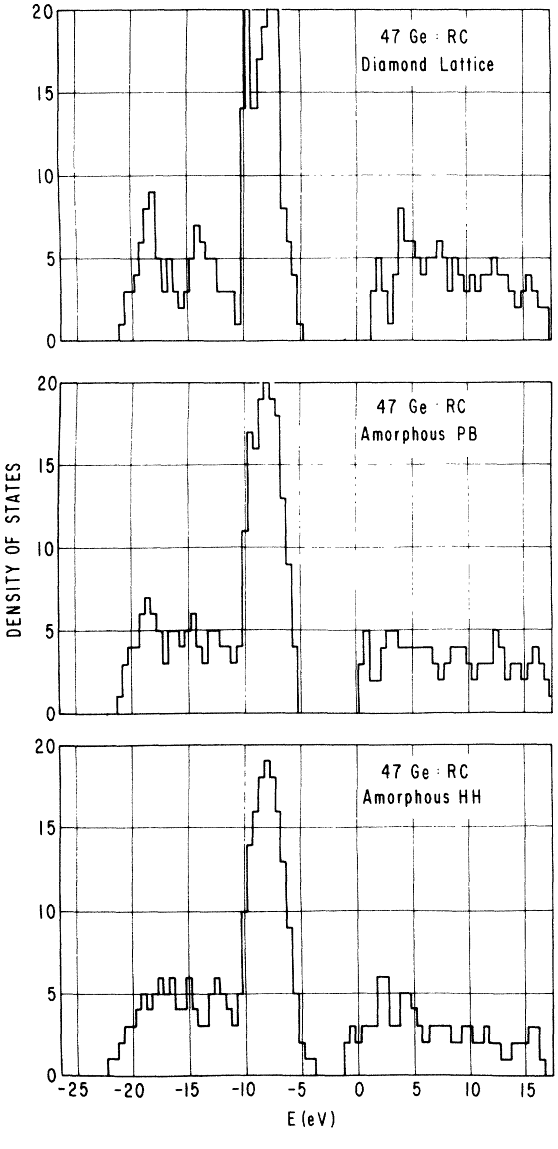

FIG. 2. Density of states of (a) crystalline (diamond) structure, (b) amorphous (Polk-Boudreaux) model, and (c) amorphous (Henderson-Herman) model, in 47-atom "ring-closing" clusters.

width is about 14.5 eV as compared to 12.0 eV in the full calculation. The largest discrepancy is the energy gap, which is far too large. A large gap has been observed in the EHT calculation of diamond, and is partially attributed to the finite cluster size and the choice of the parameter K. It has been observed in the EHT diamond calculation that states associated with the dangling bonds on the surfaces lie partly in the gap near the bottom of the conduction band and partly submerged inside the upper valence band.[8] This explains the overprominence of the peak near the top of the valence band. In spite of all these, the general features are satisfactory.

In the amorphous clusters [Fig. 1(b) and 1(c)], the sharp features of the crystalline case are generally smeared out. States start to move into the gap. The upper valence peak narrows and shifts into the gap but the top of the valence band remains relatively sharp while the bottom of the conduction bands tails a long way into the gap, especially in the HH-model cluster. The HH model is known to possess more strain than the PB model,[18] and the states in the gap in Fig. 1(c) are mainly associated with it. The branch peak in the upper valence peak seems to degenerate into a shoulder. The dip in the lower part of the valence band [Fig. 1(a)] is greatly reduced in the amorphous cases [Figs. 1(b) and 1(c)], in agreement with the experimental findings.[19]

Let us examine this dip in the lower valence band more carefully. It is known that the feature is closely associated with the number of atoms in the smallest closed rings. If we examine the outer shell of atoms surrounding our 47-atom clusters, some (about four atoms) are doubly joined to the inner ones. They are the "ring-closing" atoms, and must contribute significantly to the states in the dip. To focus on this problem, we arbitrarily take a few atoms (not ring-closing ones) in the 47 cluster and fill these ring-closing positions. The calculated densities of states are shown in Fig. 2. They represent the lower protion of the valence band more accurately, but the features in the other parts may be less satisfactory. Here, in the crystalline case, we see that the dip (Fig. 2(a)) opens up much more clearly. The corresponding PB and HH cluster calculations with these ring-closing positions filled [Figs. 2(b) and 2(c)] do not show such large dips.[20] Whether or not small dips exist in such model clusters[21] cannot be concluded from these curves.

In conclusion, EHT proves to be a simple and practical way of studying disordered systems. It can also be used to study substitutional alloys which do not involve charge transfer among the atoms. It is not difficult to extend the cluster size by using a larger computer or by sacrificing part of the time efficiency. More quantitative results can be obtained by adjusting the parameter K to fit the observed band properties and by including the d states. The nature of the states inside the gap or "pseudogap" can be examined directly by doing an electron density analysis.

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