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Comparison of the Electronic Structure of Amorphous and
Crystalline Polytypes of Ge*

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ABSTRACT

We have calculated the density of states and the imaginary part of the dielectric constant as a function of energy for four polytypes of Ge using the EPM and the tight binding model developed by Weaire. The increasing complexity of the crystal structures indicates that short range disorder is able to account well for the optical properties and density of states of amorphous Ge. Furthermore, we predict the form of the optical properties and density of states for Ge III and Ge IV.

There has been much interest recently in the density of states and optical properties of amorphous Ge¹ and Si² which can be prepared in such a way as to have a random tetrahedral network of atoms with a negligible presence of microvoids and dangling bonds.

The density of states and optical properties of these amorphous materials obtained from experiment^{1,2} show certain distinctive features that are in many cases quite different from the corresponding ones of the crystalline phases. For example the distinctive one hump form of the imaginary part of the dielectric function, $\epsilon_2(\omega)$, for amorphous Ge has no counterpart in any known crystal except for the calculation in this paper on Ge III³ (see Fig. 2b). This novel form is not well understood; however speculation has proceeded primarily along the following two directions: (1) the hump like structure is a result of an enhancement of the Λ peak in the diamond structure arising from the preservation of the tetrahedral arrangement in the amorphous state,⁴ and (2) that it is a direct consequence of long range disorder which results in a non conservation of crystal momentum and a red shift of the ϵ_2 .⁵

For the density of states, one finds experimentally the retention of a gap in the amorphous phase which has also been predicted theoretically by Weaire and Thorpe⁶, and McGill and Klima.⁷ However, the conduction band density of states for the amorphous solid has none of the structure found in the diamond case (see Fig. 1a). Furthermore the form of the valence band density of states in the amorphous solid consists of a smoothed peak at the top of the valence band and a seemingly large broad peak at the bottom of the valence band.⁸ This is in contrast to the three strong peaks found in the valence band of the

crystalline phase.

In this paper we wish to consider the following question. How much disorder is necessary to achieve the distinctive features evident in the amorphous data? To explore the possible answers to this question we have calculated the band structure and density of states for Ge in the diamond structure (GeI), hexagonal Ge (Ge2H), Ge III³ and Ge IV³ using both the Empirical Pseudopotential Method (EPM)⁹ and the tight-binding model used recently by Weaire.⁶ Using the pseudopotential band structure we have also calculated the dielectric function and reflectivity as a function of photon energy for these structures.

Ge I, Ge 2H, Ge IV, and Ge III with two, four, eight, and twelve atoms per primitive cell respectively, provide us with a set of structures which become more and more locally disordered. What we imply by local or short range disorder is that we have a crystal (long range order) and yet the atoms in the primitive cell of our crystal are in a "disordered" tetrahedral arrangement.

The results of our calculation will show that local disorder is able to account well for the optical properties and density of states for amorphous Ge. In particular we show that the peak of the ϵ_2 function is not associated with Λ transitions but rather with Σ and Δ transitions as in the diamond case and that non-conservation of crystal momentum is not a requisite for the position and qualitative form of the ϵ_2 function. However, before we discuss our results in detail we first give a brief description of the crystal structures that we have studied.

Ge 2H¹⁰ has not yet been found to exist in nature. However, it was taken to be in an ideal hexagonal structure with the same density and nearest neighbor distance (2.45 Å) as that of Ge I. Ge IV¹¹ and Ge III¹² are metastable crystalline forms of Ge which are recovered from high pressure experiments and persist at normal pressures. Ge IV has a body-centered cubic lattice and the structure is completely specified by a lattice constant $a = 6.92 \text{ \AA}$ and an internal parameter³ $x = .1$. Each linked pair of atoms has one bond of length 2.40 Å and three bonds of length 2.50 Å. The average bond length is approximately 2.48 Å. There are also two types of bond angles approximately equal to 118° and 100° respectively. All the eight atoms in the primitive cell are of one type so that they have the same relative arrangement of neighboring atoms. There is one next nearest neighbor at 3.60 Å, six at 3.73 Å, six at 4.04 Å, etc.

Ge III has a simple tetragonal lattice and the structure is specified by two lattice constants $a = 5.93 \text{ \AA}$, $c = 6.98 \text{ \AA}$ and four internal parameters³ which were taken to be $x_1 = .09$, $x_2 = .173$, $x_3 = .378$, and $x_4 = .25$. The bond lengths are all about the same length and approximately equal to 2.49 Å. The bond angles, however, are quite dissimilar. They range from about 20% less to 25% greater than the ideal tetrahedral angle (109° 28'). In this structure the Ge atoms are positioned in two different types of environment. In the primitive cell there are four atoms of type (1) and eight atoms of type (2). The atoms of type (2) form long four-fold spiral chains along the \bar{c} direction while atoms of type (1) form bonds between atoms in the different spirals. Atoms of type (1) have two next nearest neighbors at 3.45 Å,

two at 3.64 Å, two at 3.81 Å, etc. Kasper and Richards³ neglected to mention the presence of the first two pairs of next nearest neighbors. Atoms of type (2) have one next nearest neighbor at 3.45 Å, two at 3.56 Å, one at 3.64 Å, etc. Finally Ge III is unusual because of the presence of five and seven fold rings of bonds.

It is evident that Ge III has many of the properties that one would intuitively attribute to an ideal amorphous structure. That is: (i) no dangling bonds, (ii) variations in bond lengths and angle, (iii) atoms in different environments and (iv) the occurrence of five and seven fold rings. On the other hand, Ge IV is more closely associated with Ge 2H and Ge I.

The bulk densities of Ge III and Ge IV differ by less than 1%. However, they are both about 10% greater than those of Ge I and certain types of amorphous Ge.¹ Therefore, a comparison of the differences between optical properties of Ge III and Ge IV can be attributed primarily to structural and symmetry differences. Hence comparisons of the polytypes provide a method of filtering out the effects of greater density.

In Figs. 1a, b, and c, we show a plot of the density of states for Ge I, Ge IV, and Ge III respectively. Superimposed on the Ge I density of states is a sketch of the amorphous density of states obtained by Donovan and Spicer.¹ The sharp peaks are primarily due to Bragg gaps¹³ and would be smoothed out in a structure with no periodicity. Keeping this in mind we can make some interesting comparisons between these structures and we can examine the trends in going from Ge I to Ge IV¹⁴ to Ge III to amorphous.

First we notice a feature common to both Ge III and Ge IV is a smoothing out of the peaks in the conduction band found for Ge I. Next, in Ge IV we notice that the two peaks at the bottom of the valence band seem to gain more structure relative to Ge I. However, these peaks still maintain most of their individual character. For Ge III, however, there is a thorough mixing of the two peaks. This is similar to the suggestion by Thorpe et al.¹⁵ for the amorphous case. The band edges of Ge I and Ge IV are similar with gradual slopes. On the other hand, Ge III and amorphous Ge have very sharp edges. In Fig. 1c we also show an averaged Ge III density of states which agrees well with that of the amorphous case. Another interesting feature of these structures is the size of the gap. We find that Ge IV has a zero gap situated at $k = (1, 0, 0) \frac{2\pi}{a}$, whereas Ge III has a direct gap of approximately 1.4 eV situated at $k = (0.35, 0.35, 0) \frac{2\pi}{a}$ which is larger than those of Ge I and amorphous Ge. This is probably due to the influence of the large number of five and seven fold rings which would prevent the presence of low lying antibonding s-like states in the conduction band. Weaire et al.⁶ have suggested that this would happen in structures with odd numbered rings but the degree to which it might happen is shown in Fig. 1d. Here we show the density of states for Ge III using the Weaire model. The gap is considerably larger than the gap for Ge I using the Weaire model (shown by a dotted line). Although we do not expect such a large effect in the EPM case, we still expect the influence of the odd numbered rings to be important. Finally, there seems to be a relatively good matching of gross structure of the valence band of Ge III calculated using the Weaire model (Fig. 1d) and the EPM (Fig. 1c).

The large hump at the top of the valence band in Fig. 1c represents a broadening of the delta function peak shown in Fig. 1d. In fact, the number of states per atom contained in this large hump from -3.75 eV to 0 eV is precisely equal to the number of states contained in the delta function peak (2 states/atom).

In Figs. 2a and 2b we show plots of the imaginary part of the dielectric function, ϵ_2 , vs. energy for Ge IV and Ge III respectively. Superimposed on the Ge III curve is a sketch of the amorphous dielectric function obtained by Donovan et al.¹ Ge IV has two strong peaks and the overall spectrum resembles that of Ge 2H.¹⁶ In Fig. 2b we show the average ϵ_2 for Ge III obtained by a weighted average over $\epsilon_{2\perp}$ and $\epsilon_{2\parallel}$. Separately $\epsilon_{2\perp}$ and $\epsilon_{2\parallel}$ ¹⁶ have a similar one-hump structure as the averaged ϵ_2 .

The broad peak around 3.0 eV for Ge III is the result of transitions between many different bands. The strongest transitions occur mostly along the [001] direction referenced with respect to points in various regions of the Brillouin zone. For example, the main contribution at 2.85 eV comes from a thin tubular region whose axis is parallel to the [001] direction and passes through the central part of the triangular faces of the irreducible part of the Brillouin zone. The [001] direction in GeIII can be compared with certain directions in GeI where the local environment of the atoms is similar. For atoms of type (1) in GeIII the [001] direction is comparable to the [110], Σ , direction for GeI atoms, whereas for atoms of type (2) the [001] direction is similar to the [100], Δ , direction of GeI. Transitions along Δ and Σ give rise to the main ϵ_2 peak in the GeI spectrum.

The overall qualitative agreement between the ϵ_2 for GeIII and the amorphous case is quite encouraging. We have noticed that if we increase the lattice constants, the gap gets smaller, the peak moves to lower energies, and the agreement is improved.

The marked differences in ϵ_2 for GeIII and GeIV must be attributed to the fact that GeIII has such a large variety of bond orientations which also provide for the presence of five and seven fold rings in such a dense structure.

Thus it seems that short range disorder is able to adequately reproduce most of the important features of ϵ_2 in the amorphous case. It also provides a good description of the form of the density of states as one approaches the amorphous state.

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FIGURE CAPTIONS

Fig. 1. The density of states in units of states per eV per atom for different polytypes of Ge.¹⁷ (a) GeI using the EPM (solid line) and amorphous Ge¹⁸ (dashed line). The experimental amorphous curve is from T. M. Donovan and W. E. Spicer, Phys. Rev. Letters 21, 1572 (1968). (b) GeIV using the EPM. (c) GeIII using the EPM (solid line) and an averaged density of states based on this calculation (dashed line). (d) GeIII using the tight binding model used by D. Weaire, Phys. Rev. Letters 25, 1541 (1971). The delta function peak represents the top of the valence band and the dotted curve represents the position of the bottom of the conduction band in the case of GeI calculated using the Weaire model.

Fig. 2. The imaginary part of the dielectric function, ϵ_2 .¹⁷ (a) GeIV obtained from an EPM calculation. (b) GeIII obtained from the EPM (solid line) and a sketch of amorphous Ge (dashed line). The experimental amorphous curve was obtained from T. M. Donovan, W. E. Spicer, J. M. Bennett, and E. J. Ashley, Phys. Rev. B2, 397 (1970).

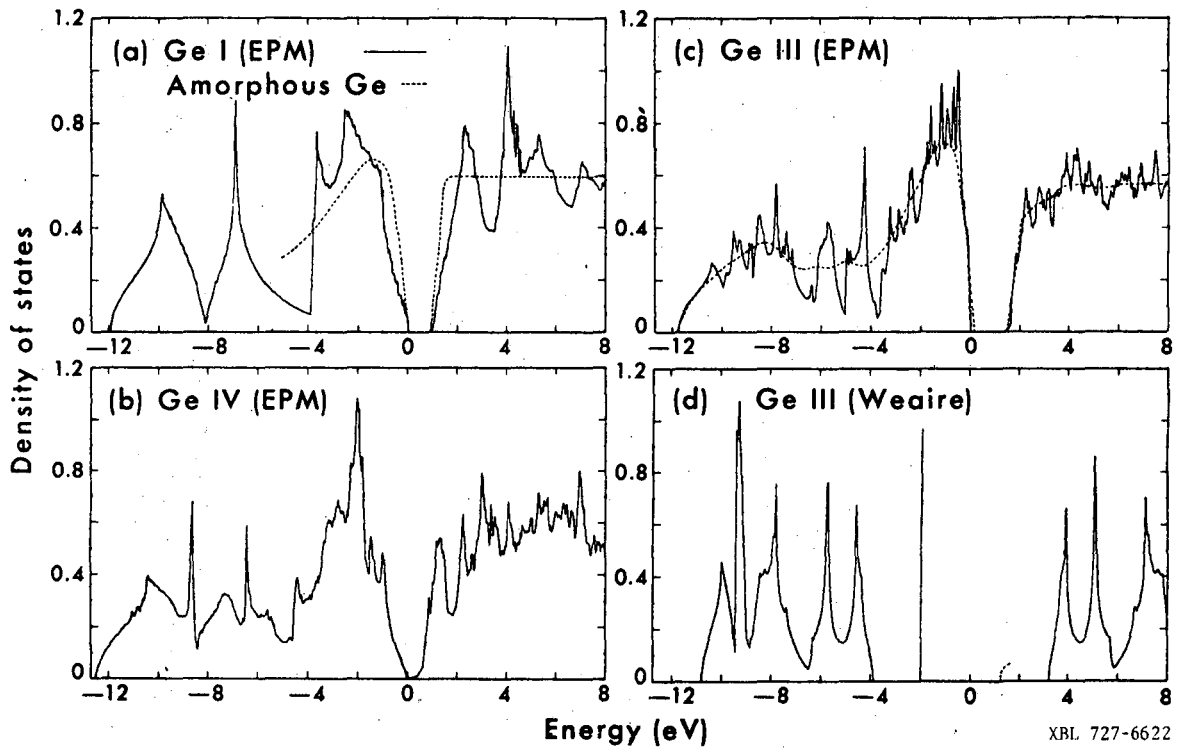


Fig. 1.

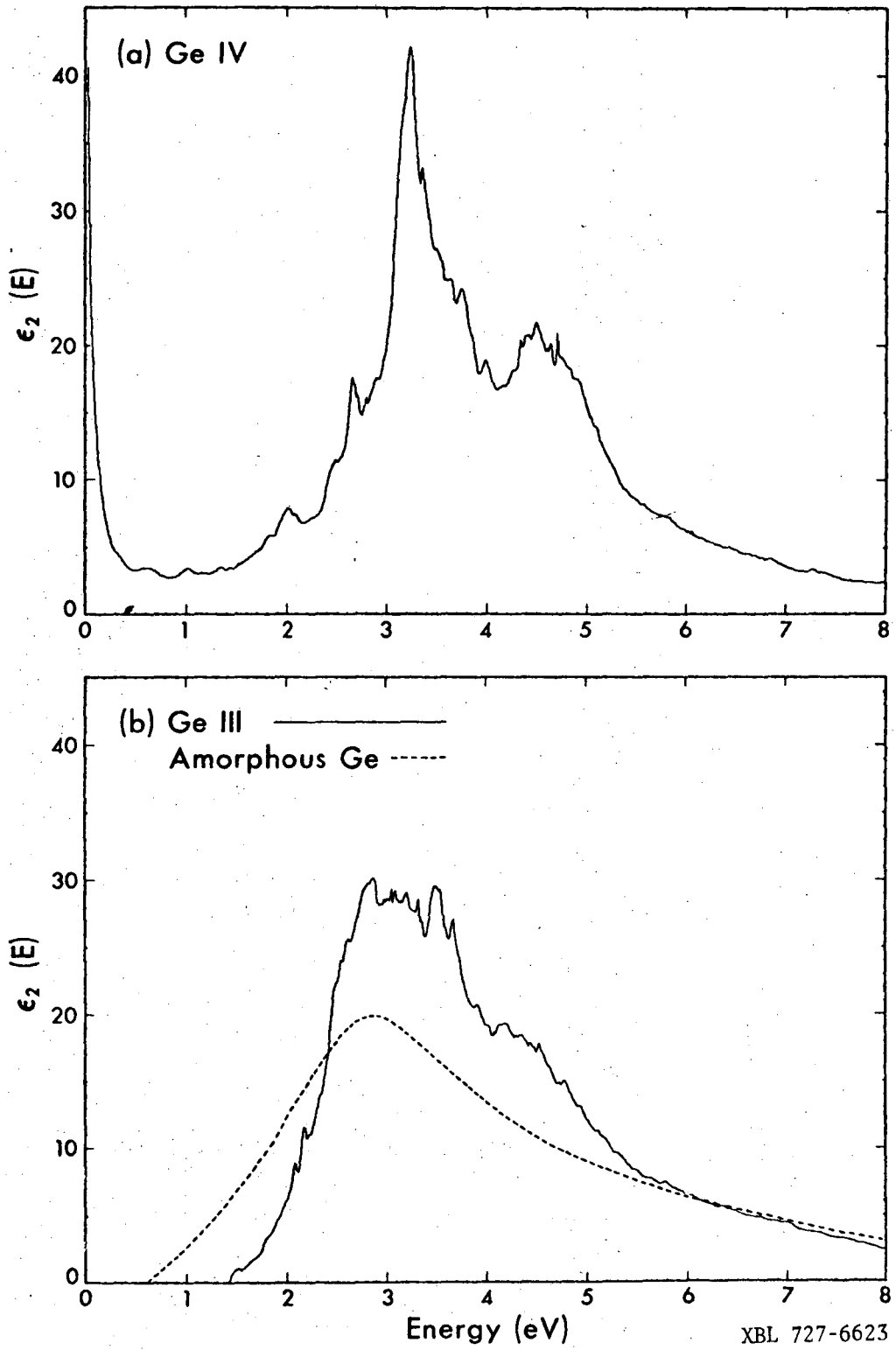


Fig. 2.

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