

⁷L. Cartz, Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem. **120**, 241 (1964).

⁸B. J. Skinner and D. E. Appleman, Amer. Mineral. **48**, 854 (1963).

⁹K. G. Denbigh, Trans. Faraday Soc. **36**, 936 (1940).

¹⁰For a review of $d\pi-p\pi$ bonding, see K. A. R. Mitchell, Chem. Rev. **69**, 157 (1969).

¹¹C. G. Dodd and G. L. Glen, J. Amer. Ceram. Soc. **53**, 322 (1970).

¹²J. J. Fahey, Amer. Mineral. **49**, 1643 (1964).

¹³Except for graphite, the bond polarizabilities have been calculated from data in standard tables. For graphite $n=2.73$ was used; this value is for light polar-

ized in the plane of the carbon rings [D. L. Greenaway *et al.*, Phys. Rev. **178**, 1340 (1969)]. Bond-order values were taken from L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N. Y., 1960), pp. 234-239.

¹⁴W. Noll, *Chemistry and Technology of Silicones* (Academic, New York, 1968), Chap. 6.

¹⁵D. P. Craig and N. L. Paddock, J. Chem. Soc. **1962**, 4118.

¹⁶O. Mugge, as quoted in W. C. Levengood, J. Appl. Phys. **30**, 378 (1959).

¹⁷S. Okabe, T. Tsumari, and T. Tabato, J. Appl. Phys. **40**, 2894 (1969).

Electronic Density of States of Amorphous Si and Ge

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The density of states of the valence and conduction bands of Si and Ge are discussed using a simple tight-binding Hamiltonian. It is shown that certain features of the density of states for the case of the diamond structure are related to the short-range order and hence should be retained in the amorphous state while others depend on long-range order and are expected to disappear.

Much recent experimental effort has been devoted to the determination of the electronic density of states of amorphous semiconductors, particularly Ge^{1,2} and Si,^{3,4} and the results so far obtained have excited a good deal of theoretical speculation on the subject.⁵⁻⁷ An accurate comprehensive theory for the electronic properties of these solids is still lacking^{8,9} and is likely to remain so for some time. However it has recently been shown^{10,11} that the problem is not wholly intractable if a simple Hamiltonian of the tight-binding type is used—in particular, it can be shown that for such a Hamiltonian there is a gap in the electronic density of states for *any* structure with tetrahedral coordination of nearest neighbors. This dispels some, if not all,¹² of the mystery surrounding the observation¹⁻⁴ of such a gap in the amorphous state. In this Letter the same Hamiltonian is used to give a discussion of the shape of the density of states for crystalline and amorphous semiconductors which hinges on a question that has long been of interest in this area but has hitherto been almost entirely unresolved. *Which features of the crystalline density of states are due to the long-range order of the structure and which are due only to the short-range order?* Only the latter are expected to be retained in the amorphous structure since this

has essentially the same short-range order as the crystal but without the accompanying long-range order. Our conclusions appear to be consistent with the evidence available at present and we suggest a measurement which should provide a critical test of the model.

Our Hamiltonian^{10,11} acts on a set of basic functions $|\varphi_{ij}\rangle$ which are the “ sp^3 ” hybridized orbitals that can be formed at each atomic site. The subscript i refers to the atom and j to the bond. Bonding and antibonding states can be formed with the four nearest neighbors of each atom that lie at the corners of a tetrahedron. The Hamiltonian contains two parameters V_1 and V_2 :

$$H = V_1 \sum_i |\varphi_{ij}\rangle \langle \varphi_{ij'}| + V_2 \sum_j |\varphi_{ij}\rangle \langle \varphi_{i'j}|; \quad (1)$$

these are, respectively, the matrix element between orbitals associated with the same atom (and different bonds) and the matrix element between orbitals associated with the same bond (and different atoms). Such a simple Hamiltonian cannot be expected to give a very accurate description of Si and Ge but it does provide quite a good qualitative description of the valence bands of these semiconductors in the crystalline state.^{11,13} Figure 1 compares the density of states calculated from this Hamiltonian for the diamond struc-

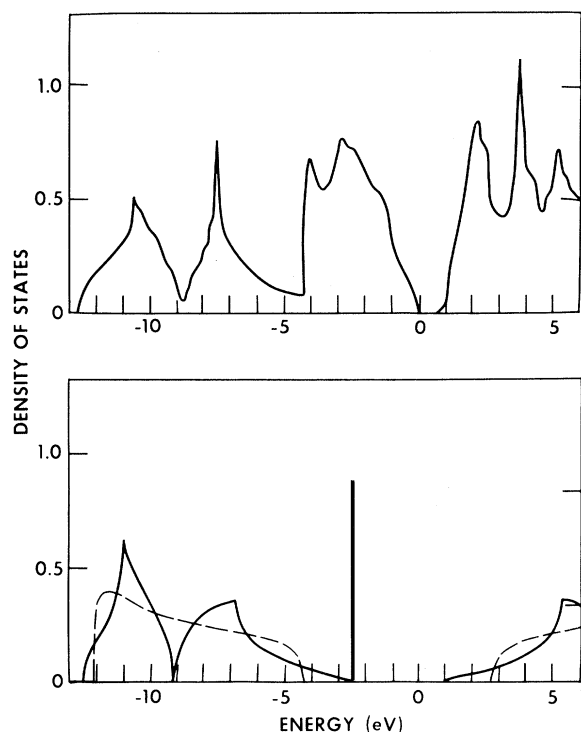


FIG. 1. Top, the density of states for Ge with the diamond structure, as calculated by Herman *et al.* (Ref. 14). Bottom, the density of states as calculated using the Hamiltonian of Ref. 10 with the diamond structure (solid line) and the Bethe lattice (dashed line). The delta function indicated by a vertical line is found in both structures. Units are states/eV atom.

ture,¹¹ using $V_1 = -2.5$ eV and $V_2 = -6.75$ eV, with that calculated for crystalline Ge by Herman *et al.*¹⁴ (For a similar diagram of a calculated density of states for Si, see Kane.¹⁵) It will be seen that the main features of the valence band are similar in our fairly crude calculation and Herman's much more sophisticated one (see also Ziman¹⁶), the principal discrepancy being the reduction of the broad peak at the top of the band to a single delta function. The delta function corresponds to a flat band in \vec{k} space. The states which contribute to this delta function are bonding p states which may be described by localized wave functions. (Such a wave function may be constructed on any closed even ring of bonds in the system by giving the basis functions amplitudes $++--++--\dots$.) By including overlap between more distant neighbors, the delta function in our calculation could be broadened and agreement with Herman's calculation would be improved. The conduction band does not correspond nearly so closely in the two calculations, since further basis functions would need to be

introduced to describe this in a tight-binding formalism.^{11,13} In particular, our model produces another delta function at the top of the conduction band¹¹ which in reality (represented by Herman's calculation with sufficient accuracy for our purposes) corresponds to bands that are spread over a wide range of energy.^{11,13} While some apology for the failure of the model to accurately describe the conduction band in the crystalline state seems in order, it should be stressed that the model does give a good description of the valence band and is the only one for which precise and rigorous statements can be made for topologically disordered (i.e., amorphous) structures at the present time.

We assume that the Hamiltonian (1) applies to amorphous systems where the details of the topology or connectivity of the amorphous structure enter through the summation in (1). We thereby neglect the random variation of V_1 and V_2 due to distortions of bond lengths and angles from ideal values of perfect tetrahedral coordination. While current structural models¹⁷ support such a viewpoint as a first approximation, the effect of the superposition of this *quantitative* disorder on the *topological* disorder which we have studied is certainly worthy of further attention. The delta function in the density of states in Fig. 1 remains even if the structure is disordered—indeed it is quite independent of the details of the structure provided that it is everywhere tetrahedrally coordinated.¹¹ The delta function and hence the broadened peak which is found in more realistic calculations are consequences of the *short-range* order (by which we mean merely the tetrahedral coordination of the nearest neighbors) and not the *long-range* order; it is not a “Brillouin-zone effect” related to the translational symmetry of the crystal. The delta function contains 2 states per atom for *all* tetrahedrally coordinated structures and the existence of even rings is not necessary¹¹ although these do provide a useful representation for the wave function in the diamond lattice.

The other peaks at the bottom of the valence and conduction bands are indeed Brillouin-zone effects, as may be neatly demonstrated by an exact calculation¹⁸ of the density of states for the Bethe lattice, also shown in Fig. 1.

The Bethe lattice¹⁸⁻²¹ is a mathematical network containing no closed loops and having a constant coordination number which in this case is 4. It has the advantage of being mathematically tractable, and may be regarded either as a purely abstract lattice having no physical counterpart,²² or

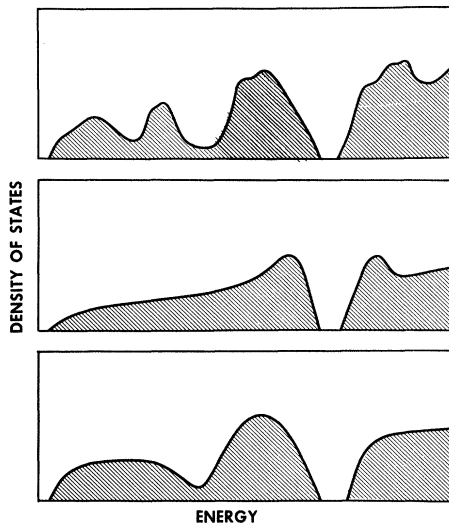


FIG. 2. Three alternative models for the density of states of amorphous Si or Ge. Top, the Brust model. Middle, the Penn-Phillips model. Bottom, the model presented here. All three sketches are schematic.

as a convenient first approximation in treating real amorphous structures.^{11, 18, 23} While the delta function in the density of states for the diamond structure remains for the Bethe lattice, the rest of the density of states is rather featureless as shown by the dashed line in Fig. 1. The two pronounced peaks in the lower half of the valence band for the diamond structure are not found here, which demonstrates that they do not result from the tetrahedral coordination and we may attribute them to the long-range order of the crystal structure. In other words, the broad peak at the top of the valence band is due to *short-range* order and should be retained in the amorphous state while those at the bottom of valence and conduction bands are related to the *long-range* order and are not expected in the amorphous state.²⁴

Figure 2 presents a sketch of the density of states expected for amorphous Si and Ge on the basis of these considerations. We have also sketched the form of the density of states as suggested by two alternative theoretical models. Brust⁶ has proposed that the crystalline density of states, calculated for a dilated crystal and broadened somewhat, is appropriate for an amorphous semiconductor. Our model shows that this is a highly questionable procedure, for although it may be reasonable for the lower part of the valence band in Fig. 1, it is surely incorrect for those states at the top of the valence band that result from short-range order.

Penn²⁵ has set up a simple isotropic model for the band structure of an amorphous semiconductor, in which the density of states diverges logarithmically on either side of the gap and is free-electron-like elsewhere. Phillips⁷ has recently advocated such a model. Of course the logarithmic divergences are assumed to be broadened into two peaks.

The three models represented in Fig. 2 are derived from rather different points of view. The one presented here may be preferable on the grounds that it is based on the study of a Hamiltonian approximating the true Hamiltonian is a well-defined way, rather than on an arbitrary *Ansatz*. That is not to say, however, that either of the other two approaches might not give a better description of the density of states. All three models would appear to be qualitatively in accord with the density-of-states picture suggested by Donovan and co-workers^{1, 2} on the basis of photoemission and optical-absorption measurements, although the fact that no evidence was found for any structure in the conduction band might be regarded as somewhat at variance with the Brust and Penn-Phillips models. All three models entail a broad peak at the top of the valence band, in keeping with the conclusions of Donovan and co-workers.^{1, 2} Clearly experimental information concerning the density of states in the lower half of the valence band would be most useful at this point. Unfortunately all the photoemission studies done so far on amorphous semiconductors¹⁻⁴ have not used photons with sufficiently high energies to probe the lower half of the valence band, because of a lack of suitable windows. Soft-x-ray emission spectroscopy, which does not appear to have been used yet to investigate amorphous Si and Ge, should provide a clear and direct indication of the shape of the density of states over the entire valence band, since it is remarkably successful in doing so for crystalline Si.²⁶ Such a measurement is therefore proposed as a critical test of the model used here.²⁷ It should not be difficult to discriminate between the three models illustrated by Fig. 2, since their implications for the shape of the valence band are quite distinct.

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¹T. M. Donovan and W. E. Spicer, Phys. Rev. Lett. **21**, 1572 (1968).

- ²T. M. Donovan, W. E. Spicer, and J. M. Bennett, *Phys. Rev. Lett.* **22**, 1058 (1969).
- ³C. W. Peterson, J. H. Dinan, and T. E. Fischer, *Phys. Rev. Lett.* **25**, 861 (1970).
- ⁴D. T. Pierce and W. E. Spicer, *Phys. Rev. Lett.* **27**, 1217 (1971); T. E. Fischer and M. Erbudak, *Phys. Rev. Lett.* **27**, 1220 (1971).
- ⁵F. Herman and J. P. Van Dyke, *Phys. Rev. Lett.* **21**, 1575 (1968).
- ⁶D. Brust, *Phys. Rev. Lett.* **23**, 1232 (1969).
- ⁷J. C. Phillips, *Phys. Status Solidi (b)* **44**, K1 (1971).
- ⁸M. H. Cohen, *J. Non-Cryst. Solids* **4**, 391 (1970).
- ⁹N. F. Mott, *Comments Solid State Phys.* **3**, 123 (1971).
- ¹⁰D. Weaire, *Phys. Rev. Lett.* **26**, 1541 (1971).
- ¹¹D. Weaire and M. F. Thorpe, *Phys. Rev. B* **4**, 2508 (1971).
- ¹²J. C. Phillips, to be published.
- ¹³D. Weaire, M. F. Thorpe, and V. Heine, to be published.
- ¹⁴F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Brown University, 1967*, edited by D. G. Thomas (Benjamin, New York, 1968), p. 503.
- ¹⁵E. O. Kane, *Phys. Rev.* **146**, 558 (1966).
- ¹⁶J. M. Ziman, to be published.
- ¹⁷D. E. Polk, *J. Non-Cryst. Solids* **5**, 365 (1971).
- ¹⁸J. F. Nagle, J. C. Bonner, and M. F. Thorpe, *Phys. Rev. B* (to be published); M. F. Thorpe and D. Weaire, *Phys. Rev. B* **4**, 3518 (1971).
- ¹⁹H. A. Bethe, *Proc. Roy. Soc., Ser. A* **216**, 45 (1935).
- ²⁰C. Domb, *Advan. Phys.* **9**, 245 (1960).
- ²¹L. Onsager, J. Nagle, M. S. Chen, and J. C. Bonner, to be published.

²²The theorems of Refs. 10 and 11 concerning bounds on the density of states are valid for the Bethe lattice but careful consideration of boundary conditions is necessary in this case. See Refs. 18 and 21.

²³This approximation sums all of the "Cayley trees" in a Green's-function formalism. See Ref. 20.

²⁴The second of these conclusions is somewhat weaker than the first, resting as it does on the assumption that the order of the amorphous structure beyond the tetrahedral coordination (i.e., the existence of fivefold and sixfold rings, etc.) has little effect on the density of states. Further investigation of this aspect of the problem would necessitate a more accurate characterization of the amorphous structure as well as further theoretical developments.

²⁵D. Penn, *Phys. Rev.* **128**, 2093 (1962).

²⁶G. Wiech, in *Soft X-Ray Band Spectra and the Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, New York, 1968), p. 59.

²⁷After submission of this work for publication, we have been informed that G. Wiech and E. Zöpf have just completed the experiment which we propose. The $L_{2,3}$ emission spectrum (indicative of the s -like part of the valence-band density of states), which had two peaks in the crystalline case (Ref. 26), has one broad peak in the amorphous case. The peaks correspond to the lower two peaks in Fig. 1. The peak at the top of the valence band, which is seen in the $K\beta$ emission spectrum (indicative of the p -like part of the density of states), survives essentially unaltered in the amorphous solid, as predicted by our model. See G. Wiech and E. Zöpf, in *Proceedings of the International Conference on Band-Structure Spectroscopy of Metals and Alloys*, Glasgow, September 1971 (to be published). We are indebted to Dr. D. Nagel for this information.

Nonexistence of Magnetic Ordering in the One- and Two-Dimensional Hubbard Model

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It is shown that for nonzero temperature, Hubbard's narrow-energy-band model is neither ferromagnetic nor antiferromagnetic in one and two dimensions.

The Hubbard model¹ for the description of electron correlation in a narrow energy band has been of great theoretical interest for the last few years. The model retains only that part of the electron-electron interactions which arises as a result of the repulsion between two electrons of opposite spins located at the same site. In spite of this simplifying assumption, the model remains essentially a many-body problem and an exact solution cannot be found in the general three-dimensional situations. The one-dimensional problem with nearest-neighbor electron transfer has been solved exactly by Lieb and Wu,² who obtained the ground-state energy, the wave function, and the chemical potential for the system. In three dimensions Nagaoka³ considered the case of nearest-neighbor hopping and has discussed the ferromagnetism of various lattices for a nearly half-filled band. Apart from these, not many exact results are known for the model.

In this work we demonstrate explicitly the impossibility of the existence of spontaneous ferromagnetic or antiferromagnetic ordering for this model in one and in two dimensions at an arbitrary nonzero