Theory of amorphous semiconductors

A band model of disordered materials has some of the gross features of crystalline structures, with significant detailed differences.

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"Potential" is the word that first comes to my mind in thinking about the field of amorphous semiconductors. The field is potentially very large because of the wide range of phenomena and materials it encompasses. The phenomena lend themselves to a multitude of potential technological applications (see box). What I am concerned with here, however, is the challenge offered by amorphous semiconductors to our theoretical understanding.

The current theoretical status is similar to that of crystalline semiconductors 15 to 20 years ago when the first major advances in the band theory of crystals were made. Band theory built on the universal features of the electronic structure of crystals. Although amorphous semiconductors by contrast are examples of disordered materials (see figure 1), they should also possess such universal features. Experiments on amorphous semiconductors probe just those aspects of electronic structure of disordered materials that differ most from the corresponding aspects of those of crystals. Theory and experiment on amorphous semiconductors are therefore very illuminating with respect to the larger subject of the electronic structure of disordered materials.

In an amorphous material the atoms may have some local organization or short-range order, but lack the periodic structure, that is, long-range order, of crystals over distances greater than a few atomic radii. The most important elements that exhibit such behavior are silicon and germanium from Group IV of the periodic table, arsenic, antimony and bismuth from Group V and sulfur, selenium and tellurium from Group VI (the chalcogenides). Other elements drawn from all over the periodic table may be present as well, usually as minority constituents.

These elements form a variety of covalent amorphous structures that have excellent short-range but no long-range order. They may be single elements such as bulk selenium, tellurium or even boron, or films of silicon or germanium; they may be compounds such as arsenic tritelluride, or they may be multicomponent alloys that form bulk glasses over a broad range of composition. In crude outline the arrangements of atoms or molecules vary from those that are primarily linear in character for the Group VI elements towards planar structures as Group V elements are added and then towards three-dimensional network structures as Group IV elements are added.

It is convenient to represent such a wide variety of materials and structures by a single model. Sir Nevill Mott[1] first defined an ideal covalent glass as a one, two or three-dimensional random network with excellent short-range and no long-range order. Every atom has its valence requirements locally satisfied; there are no dangling bonds, nor other structural defects. Such a model was proposed by R. Grigorovici and his colleagues for amorphous germanium and successfully constructed by David Turnbull and his associates. The model was also used by Simon C. Moss and Jozef F. Graczyk[2] to interpret electron diffraction measurements on amorphous silicon films.

Experimental facts

Let us single out a few basic experimental facts regarding amorphous semiconductors. The electrical conductivity σ appears to be primarily intrinsic in its temperature dependence even for alloys of varying valence and widely different composition. It has the form

$$\sigma = \sigma_0 e^{-\Delta E/kT}$$

over a wide range of temperatures T. The pre-exponentials σ_0 can be an order of magnitude or more smaller than for crystals, but the activation energies ΔE are of comparable size.

This activated temperature dependence implies the existence of a band gap. The observation of a definite energy limit in the optical absorption by amorphous semiconductors carries the same implication. The energy dependence of the imaginary part of the dielectric function ϵ_2 is broadly similar in a (amorphous) and c (crystalline) forms of the same material, apart from a loss of structure in the a case.

Other measurements further indicate that these materials act as low-mobility intrinsic semiconductors. The thermoelectric power is usually positive and its

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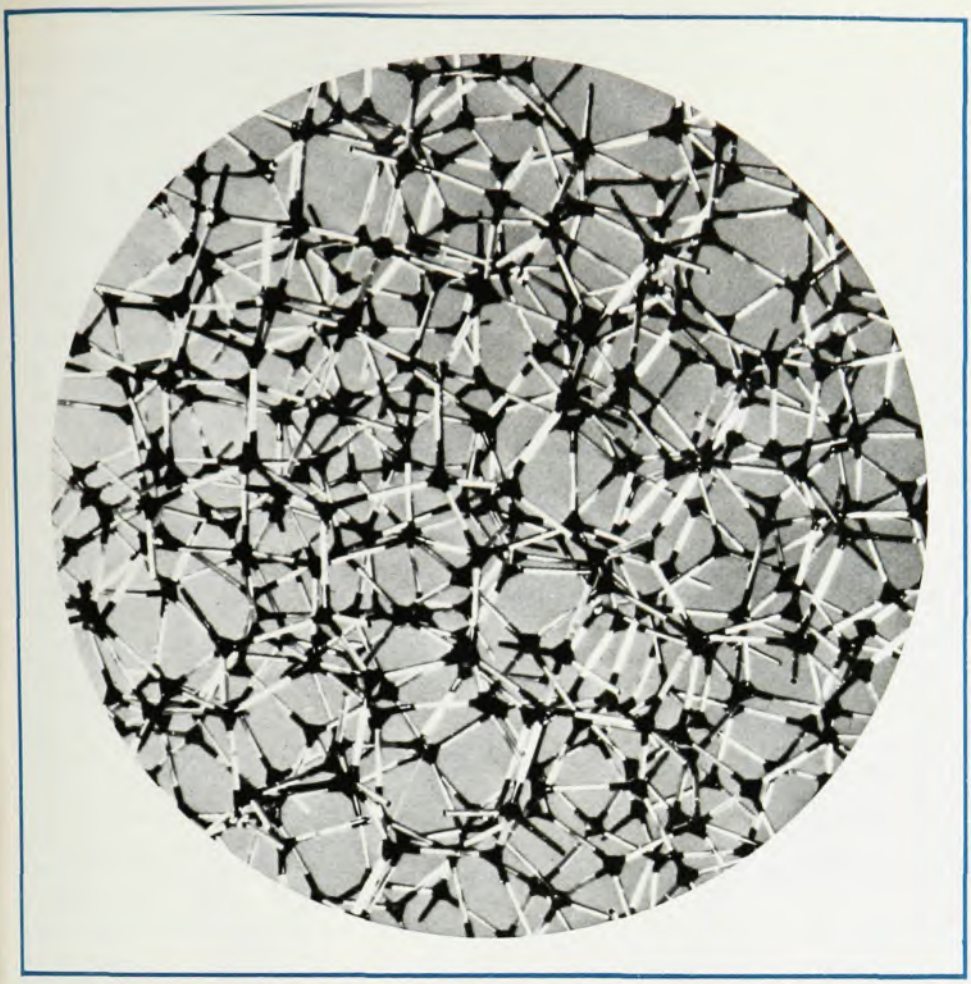


Structural model for amorphous germanium or silicon. The three-inch rods in the model represent 0.235-nanometer bonds in silicon and 0.245-nm bonds in germanium. Donald E. Polk of Harvard, who built this model, describes its details in a forthcoming issue of *J. Non-Crystalline Solids*.
Figure 1

magnitude normal. The Hall constant is usually negative and small. Hopping conduction may occur at low temperatures or high frequencies.

The gross features of the atomic and electronic structures of these materials should be dominated by the covalent bonding requirements of their constituents. Therefore the short-range order in *a* materials is expected to be similar to that in corresponding or related crystals, as the above observations confirm. There should be valence and conduction bands in the *a* materials similar to those of crystals, as the behavior of electrical conductivity and dielectric constant imply. Finally, the behavior of electrical conductivity in the alloys indicates that they are nearly ideal glasses; almost all of the valence electrons are tied up in bonds.[1,3]

Basic band model

A quantitative interpretation of the experimental data requires a detailed model of the electronic structure of disordered materials. We start by noting that in all crystals the electronic structure has certain universal features: The individual electrons are described by Bloch wave functions that are extended, with long-range order in both phase and amplitude, and the corresponding energies fall into bands of allowed levels that are separated by gaps and have sharp edges. We assume that disordered materials also possess such universal features.

The basic band model (BBM), synthesized by Mott[1] out of earlier work, is the simplest possible representation of such universal features. The model assumes a band of extended states with long-range order in their amplitudes but only short-range order in their phases.

Devices: What progress?

Two years ago, amorphous semiconductors were the subject of intense debate. On one side, advocates were claiming that a multitude of devices, building on the switching properties of these materials, would revolutionize the electronics industry. On the other side, opponents argued that practical and reliable devices made from amorphous materials were technologically impossible.

Has the passage of time and subsequent research settled the issue? So far only one device is currently being produced and sold; the other promised devices are still in the development stage. This device is a "read mainly" memory, to be distinguished from "read only" memories because they can be used for some write operations as well. Several customers are presently evaluating the 256-bit memories, so no statements can yet be made as to the reliability and quality of the memories. However, the company producing them guarantees 1000 write operations.

Although opinion is still divided on the issue, the storm of debate has subsided into a period of calm waiting. The only proof can be the actual performance of the devices. In addition a committee of the National Academy of Sciences is currently preparing a report on the fundamental properties of amorphous semiconductors. This report may provide a neutral assessment of the technological potential of these materials. —*Barbara G. Levi*

Glossary

Extended and localized states: extended states are quantum mechanical states of motion in which an electron may be found anywhere within a region of a material of linear extent equal to that of the material itself. In localized states the motion is restricted to a region of linear extent smaller than that of the material.

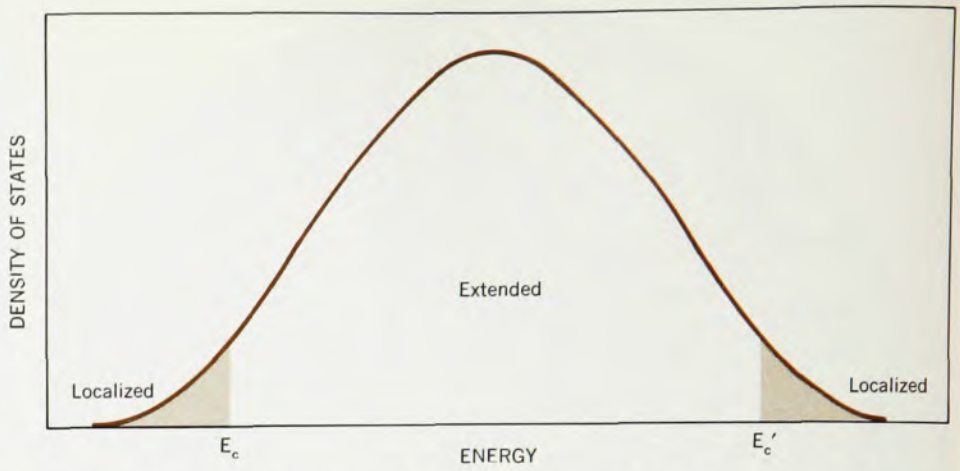
Thermopower: a measure of the voltage induced in a conductor by a temperature.

Hall constant: a measure of the voltage induced in a conductor at right angles to the current flow by a magnetic field.

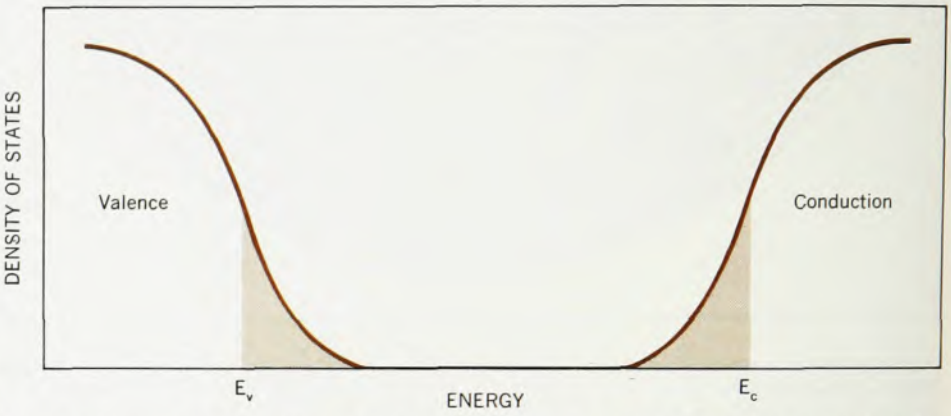
Hopping conduction: electrical conduction by occasional hopping of an electron from one localized state to a neighboring one.

Indirect gap: the difference in energy of the top of the valence band and the bottom of the conduction band of a crystal when these do not occur at the same place in wave vector space.

Percolation theory: the theory of movement or flow through a random medium, parts of which are inaccessible to the moving entity (as in a coffee pot).



In the basic band model an isolated band consists of extended states with tails of localized states above and below the energies E_c and E_c'. Figure 2



Conduction and valence bands must be added to the basic band model to describe amorphous semiconductors. The band edges have tails below the conduction-band energy E_c and above the valence-band energy E_v. Figure 3

Figure 2 illustrates the model for a single isolated band. The band has tails of localized states, which have only short-range order. There are sharp transitions at the energies E_c and E_c' from localized to extended states and vice versa.

Extensions of the model

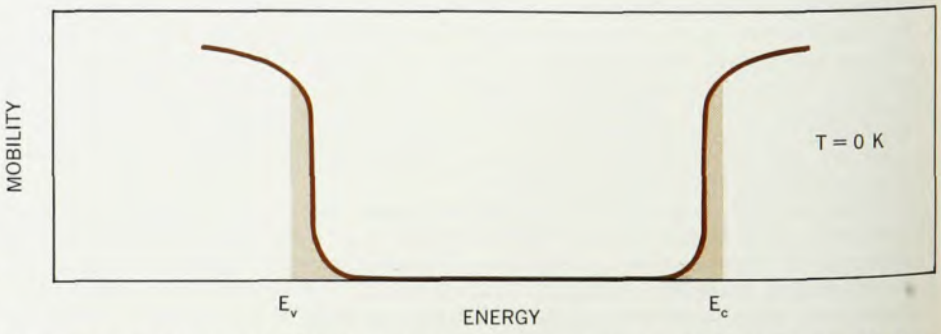
Before the basic band model can be applied to discussions of amorphous or liquid semiconductors it must be extended to include the band structure illustrated in figure 3. There is a valence band with a tail of localized states above the valence-band energy E_v and a conduction band with a tail below the conduction-band energy E_c. This structure is a generalization of the two-band model proposed by Alan H. Wilson in 1930. We can now calculate the electrical conductivity using the following equation

$$\sigma = \sum_{b=c,v} \int dE\, n_b(E) e \mu_b(E) f_b(E)$$

Here b is a band index with c labelling the conduction and v labelling the valence band; $n_b(E)$ is the density of states; $\mu_b(E)$ is the probability of occupation for a state of energy E by a hole in the valence band or an electron in the conduction band.

In crystals the sharp edges of the bands lead to the well defined activation energy observed in the electrical conductivity. Because the bands in amorphous materials have tails, one would not expect to get a sharp activation energy in this case. Clearly the simple band model needs extending. Hellmut Fritzsche, Stanford Ovshinsky and I[3] added the picture of the mobility illustrated in figure 4.

Because of the change in the nature of the states at the conduction-band and valence-band energies the mobility should fall there by several orders of magnitude; it should dip from values characteristic of transport by means of extended states to those characteristic of phonon-assisted hopping conduction in localized states. Thus the mobility has sharp cut-offs at the valence- and conduction-band energies E_v and E_c, which will give rise to a sharp value of activation energy in the above equation. The activation energy thus relates to a mobility gap rather than a gap in the



The mobility has cut-offs at valence and conduction mobility edges E_v and E_c that give rise to a sharp activation energy in electrical conductivity. Figure 4

density of states; the latter would be more pertinent to optical absorption. The energies E_v and E_c are thus mobility edges.

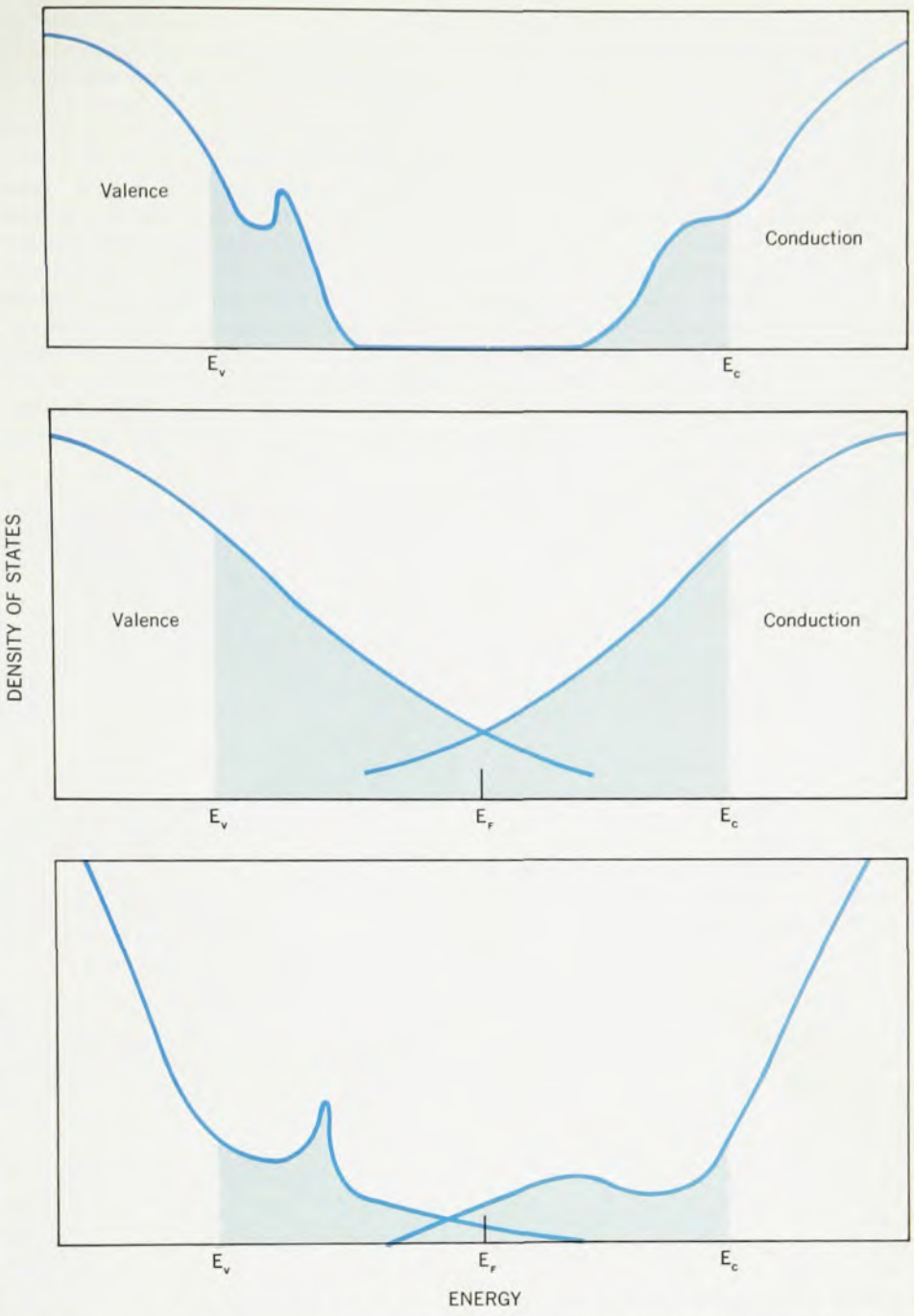
The simple band model should apply to elemental or compound glass in the ideal glassy structure. Terence F. Donovan and William Spicer[4] have measured the optical absorption of clean amorphous films of germanium of varying densities. They have found a sharp absorption edge, the energy of which increases toward the indirect gap of the crystal as the densities approach that of the crystal. These results indicate that the denser films are approaching an ideal glassy structure. Moreover, theories such as the fluctuation theory of the energy bands to be discussed below strongly suggest that well defined limiting energies in the spectrum are associated with well defined limiting configurations of the material. In the case of amorphous germanium, the only limiting configuration is the crystal. We therefore associate the well defined absorption limit occurring at the crystalline indirect-gap energy with regions of the network in which the short-range order approaches that of the crystal over a range considerably larger than average. Any disorder within the ideal network, such as bond length and angle changes, will increase the energy gap.

Walter E. Spears has found a temperature dependence of the drift mobility of carriers injected into amorphous silicon films that indicates that the tail ends about 0.2 eV below the conduction-band mobility edge in his films.[5] Because silicon films prepared in the method used by Spears often have density deficiencies of the order of 15%, only half of which anneals out, these films may have considerably greater disorder than the films studied by Donovan and Spicer. For the latter films, the tail can be expected to end considerably nearer the mobility edge.

Actual specimens of the elements and compounds do not in general have an ideal glassy structure. Because the network is well defined, it can have well defined defects such as chain ends, vacancies, dangling bonds, voids, impurities at specific sites and so forth. These defects can be expected to lead to nonmonotonicity in the density of states, so that the density of states might look like figure 5a.

The alloys are probably significantly more disordered than the elements or compounds. There is here a compositional disorder in addition to the lack of long-range translational order. In order to satisfy the local valence requirements, the connectivity of the network must change randomly, and local disorder is consequently increased. This disorder is expected to broaden the tails until they overlap, as shown in figure 5b, even if the network remains nearly ideal.[3] Such overlapping may also be present in some liquid semiconductors because of their reduced short-range order and in films deposited too rapidly or at too low a temperature for structural adjustment towards the ideal to occur. It is interesting that liquid tellurium selenide and tellurium sulfide alloys exhibited, in studies conducted by Busch and his colleagues, switching behavior similar to that observed by Ovshinsky in solid alloys.

A band model that synthesizes all of the features thus far introduced is shown in figure 5c. It has nonmonotonicity from specific imperfections and some overlap from increased randomness in nonideal structures. The peaks in the density of states as well as the states near the Fermi energy E_F would be important for the carrier kinetics. Hopping conduction would occur at the Fermi energy; this is consistent with observations at high frequency and low temperature.



Defects and imperfections in actual specimens. The irregular appearance of the tails in the density of states (a) is caused by such imperfections in the ideal glassy structure. Overlapping tails (b) can result from increased disorder in covalent amorphous alloys and some liquids. A band model for nonideal glassy semiconductors (c) must incorporate all these observed features. Figure 5

Theoretical foundations

Underlying the basic band model and its elaborations are nine assumptions:

1 Covalent glasses are nearly ideal.

2 They possess distinct valence and conduction bands with—

3 tails of localized states,

4 bodies of extended states and—
5 sharp energies of transition E_v, E_c.
6 These band energies are mobility edges.
7 The tails overlap for sufficiently disordered materials: solid alloys, liquids, bad films and so on.
8 The overlapping tails retain the parentage, or identity of bands to which the localized states belong.[6]
9 Empty valence states are positively charged and full conduction states are negatively charged even in the region of overlap of the tails. This property leads to a distribution of charged traps near the Fermi energy.

These assumptions have received varying degrees of attention and only a few of them can be regarded as firmly established. Complete justification of 1 and 2 based on first principles is far beyond our present grasp. Assuming them permits considerable progress to be made on the next four. I shall discuss these four in terms of simple model systems. I must then assert in addition that:
10 Assumptions 3 through 6 are universal features of the electronic structure of disordered materials.

Two of these four assumptions are well established. The existence of tails of localized states in disordered materials has long been argued[7-13] with increasing mathematical rigor.[12,13] The existence of bands of extended states with a finite range of coherence approximately equal to the mean free path was implicit in the pioneering work of Felix Bloch in 1929. The remaining theoretical problems are therefore to explain why there should be sharp transitions and mobility edges at the conduction and valence-band energies.

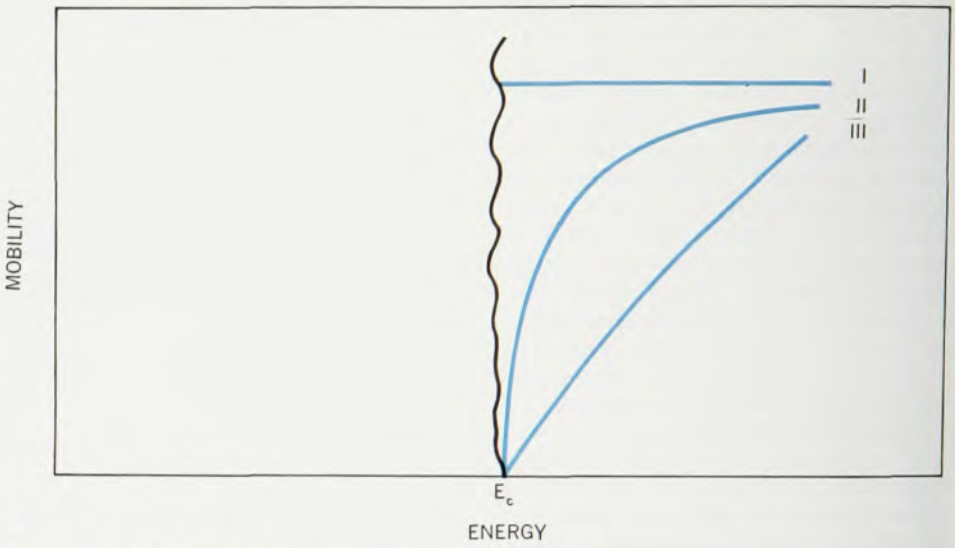
The resolution of both problems rests on the fundamental work of Philip Anderson in 1958.[14] Anderson proved that all states in a band are localized and that no diffusion occurs; that is, the mobility is zero for all energies, when the randomness becomes sufficiently great. Mott[1] recognized in 1967 that Anderson's results also implied transitions from localized to extended states at specific energies within the band at lower degrees of randomness. He synthesized this implication with the arguments supporting the existence of tails into the basic band model.

Concerning the detailed theoretical arguments, Anderson's work was far ahead of its time and suffered from a lack of subsequent conceptual clarification and technical advances. As a result it is a difficult and messy paper. In recent years, John M. Ziman,[15] David J. Thouless[16] and Elefterios N. Economou and I[17] have clarified his presentation and made his mathematical argument more precise. At present there is no doubt that the Anderson theory of localization and the BBM are correct. However, the mathematics could be further improved. Approximate calculations of the positions of the mobility edges in simple systems are now becoming available.[18,19]

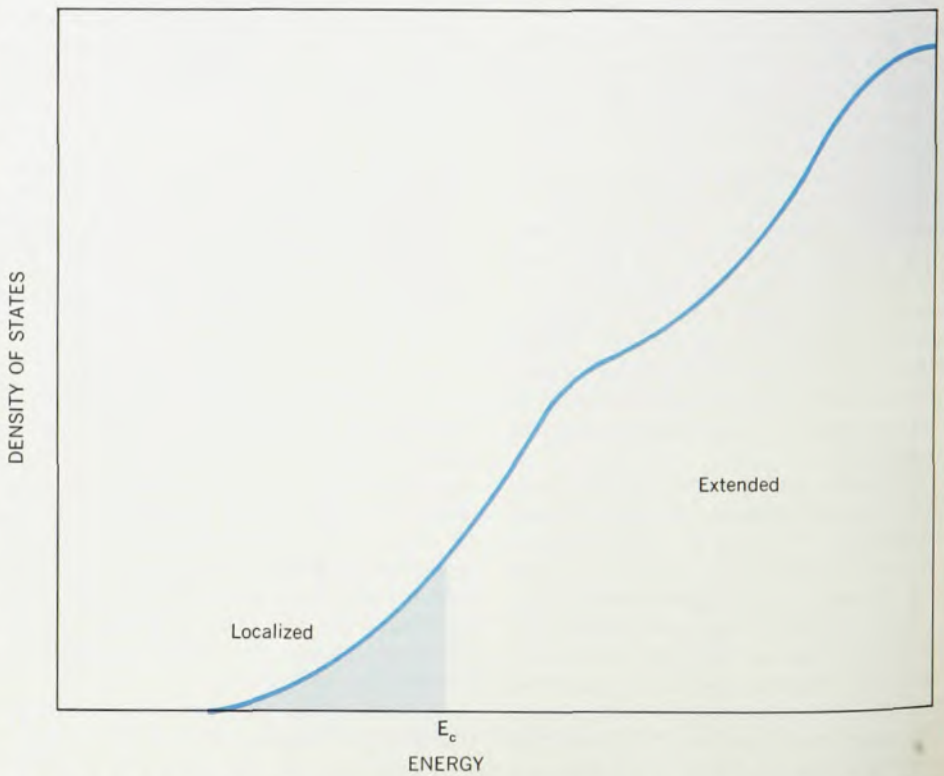
Behavior of mobility?

There is an interesting problem concerning the energy dependence of the mobility inside the mobility edges, knowledge of which is essential for a theory of the pre-exponential in the electrical conductivity, σ_0. The alternatives are depicted in figure 6 for 0 K; at finite temperatures the differences are not so marked. Case I is favored by Mott on the basis of theoretical and empirical arguments. I prefer either case II or case III, but I feel that case II is somewhat more probable on purely theoretical grounds.[18]

Consider an electron moving semiclassically in a random potential $V(r)$. Thomas P. Eggarter and I[18] have made arguments that can be generalized to give the density of states sketched in figure 7. There will be a tail of localized states below some energy E that depends in detail on the particular potential. The origin of the various states is shown in figure 8. For an energy E, space is divided into prohibited regions P where $V(r) > E$ and allowed regions A



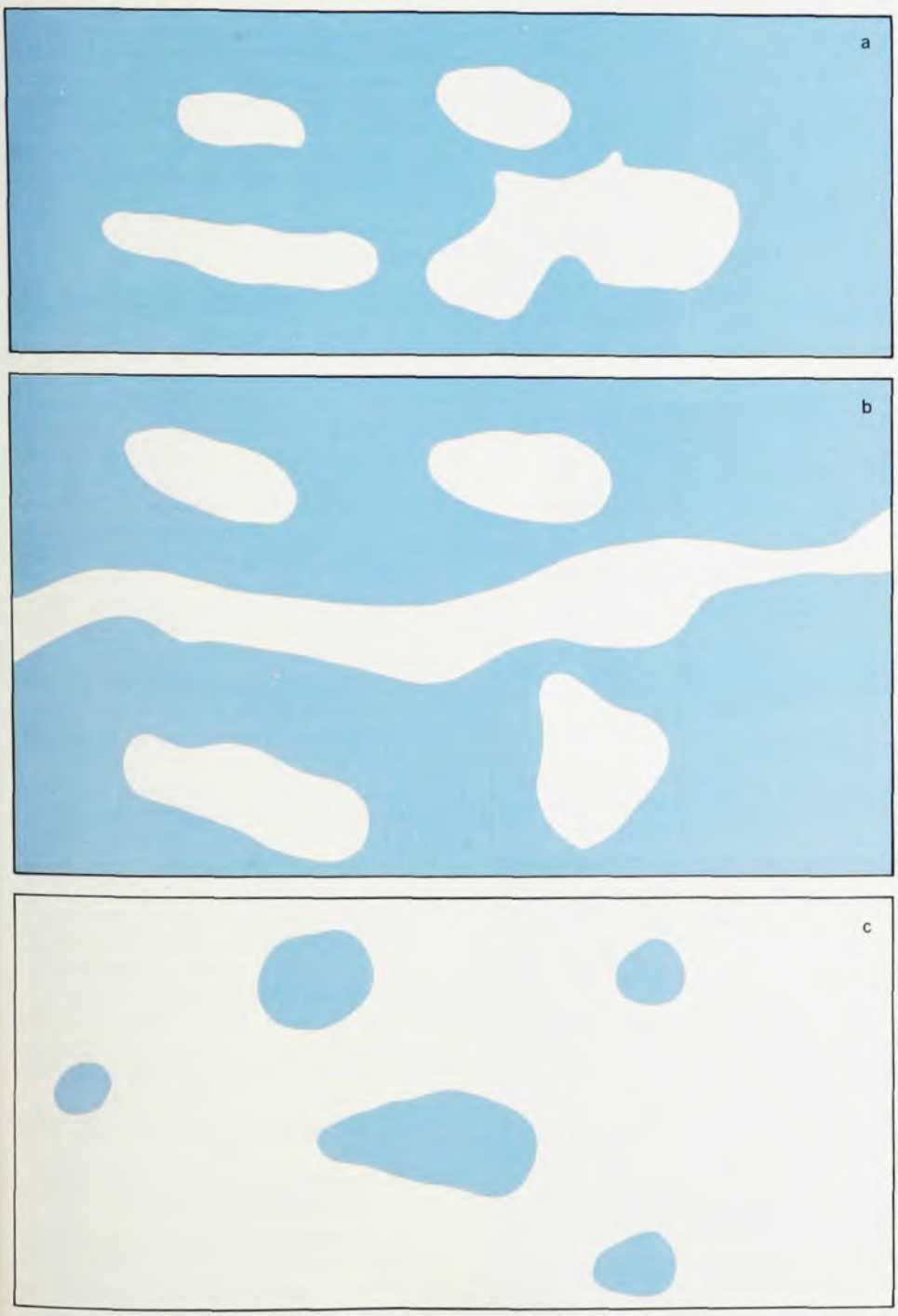
Three possible shapes for the mobility as a function of energy above the conduction-band energy E_c at a temperature $T = 0$ K. Figure 6



Density of states for an electron moving semiclassically in a random potential. The shape of the tail of localized states depends on the particular potential. Figure 7

where $V(r) < E$. Percolation theory shows that for energies below a critical energy, E_c, the allowed regions are localized and disjoint like those in figure 8a. For larger energies, a finite fraction of the space is occupied by percolation channels extending one dimensionally across the entire space as in figure 8b. As the energy continues to increase the prohibited regions shrink as shown in figure 8c and finally disappear.

The semiclassical argument can be converted into a quantum-mechanical argument by allowing for zero-point energy within the allowed regions and tunneling from one allowed region to another. The effect of the zero-point energy is simply to shift the density curve and conduction-band energy upward in energy and to change slightly the shape of the density of states. The effect of tunneling is to increase the range of the localized states somewhat without destroying localization below the critical energy. At and above this energy all localized states are converted into extended states by means of tunneling into the nearest percolation channel. However, there are now two classes of extended state just above the critical energy: resonant, or those associated primarily with localized allowed regions, and channel, or those associated primarily with percolation channels.



For an electron moving semiclassically in a random potential, space is divided into prohibited regions (color) and allowed regions (white). The prohibited regions shrink as the energy increases from below the critical energy E_c (a) to just above (b) and then way above (c). At E_c, the first extended channel appears (b). Figure 8

Semiclassically the mobility is closely proportional to the percolation probability. If, as some numerical studies indicate, this probability increases linearly with energy above the conduction-band energy, the mobility should assume the shape of case III. However, further numerical studies have suggested that the percolation probability may have critical index behavior. Then the mobility should look like case II. The quantum-mechanical mobility probably increases faster with energy than the percolation probability because of tunneling but would not change the dependence away from that of case II.

Several more facts and demonstrations lead me to prefer the mobility shape of case II. First of all, the percolation transition is like a phase transition; so is the transition at the critical energy or mobility edge in the wave function from states with only short-range order to states with long-range order in the amplitude. Secondly, recent unpublished work by Samuel F. Edwards on Green's functions supports the critical index behavior of percolation probabilities. Finally, percolation, tunneling and resonance arguments imply that the wave functions are nearly real above the conduction-band energy. I thus propose that at 0 K

$$\begin{aligned} \mu &\propto (E - E_c)^s && s < 1, E > E_c \\ &= 0 && E < E_c \end{aligned}$$

The limit $s \to 0$ corresponds to case I, which is favored by Mott. He obtained his result from a general formula for the mobility, due to Ryogo Kubo, by supposing that (a) the phase of the electronic wave function was random at each atomic site and (b) its amplitude was comparable at each atomic site. It is the latter that is contradicted by the percolation arguments and which leads to the discrepancy between cases I and II or III.

Remaining problems

I now close by commenting briefly on some outstanding problems that must be solved before we can approach the experimental results with more confidence. First we must settle the energy dependence of mobility near the conduction band energy at 0 K, then make an approximate calculation of the magnitude of the mobility. This work should next be extended to nonzero temperatures and frequencies so that hopping conduction can be included. Calculation of the optical absorption and the thermopower are problems of comparable complexity. However, the Hall constant and magnetoresistance are more difficult and should be considered later.

Many other topics need further study:

- the nature of localized states
- the role of the electron–electron interaction
- the effect of interactions between charged localized states in the region of tail overlap[20]
- the question of parentage
- the occupancy of localized states, that is, whether a localized state can be doubly occupied or whether two overlapping states can be simultaneously occupied.

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References

1. N. F. Mott, Adv. Phys. **16,** 49 (1967).
2. S. Moss, J. F. Graczyk, *Proceedings* of the Tenth Int. Conf. on the Physics of Semiconductors, Cambridge, Mass. Aug. 1970. (Published by USAEC, division of Technical Information).)
3. M. H. Cohen, H. Fritzsche, S. R. Ovshinsky, Phys. Rev. Lett. **22,** 1065 (1969).
4. W. E. Spicer, T. M. Donovan, *Proceedings* of the Tenth Int. Conf. on the Physics of Semiconductors, Cambridge, Mass. Aug. 1970. (Published by USAEC, division of Technical Information.)
5. W. E. Spears, to be published.
6. G. Srinivasan, M. H. Cohen, J. Non-crystalline Solids, to be published.
7. H. Fröhlich, Proc. Roy. Soc. A, **188,** 521 (1947).
8. A. I. Gubanov, *Quantum Electronic Theory of Amorphous Conductors (1963)*, Consultants Bureau, New York, (1965).
9. L. Banyai, *Physique des Semi-conducteurs*, Dunod, Paris (1964).
10. I. M. Lifshitz, Adv. Phys. **13,** 483 (1964).
11. V. L. Bonch-Bruevich, Fizika tuerd. Tela, **5,** 1852 (1964). Translated in: Sov. Phys. Solid State **5,** 1353 (1964).
12. B. I. Halperin, M. Lax, Phys. Rev. **148,** 722 (1966).
13. J. Zittartz, J. S. Langer, Phys. Rev. **148,** 741 (1966).
14. P. W. Anderson, Phys. Rev. **109,** 1432 (1958).
15. J. M. Ziman, J. Phys. C **2,** 1230 (1969).
16. D. J. Thouless, to be published.
17. E. N. Economou, M. H. Cohen, to be published.
18. T. P. Eggarter, M. H. Cohen, to be published.
19. E. N. Economou, S. Kirkpatrick, M. H. Cohen, T. P. Eggarter, Phys. Rev. Lett. **25,** 520 (1970).
20. G. Srinivasan, to be published. □