8 September 1978, Volume 201, Number 4359 SCIENCE

Electrons in Glass

Nevill Mott

The manufacture of glass, along with the forming of metals, is an art that goes back to prehistoric times. It always seems to me remarkable that our first understanding of the ductility of metals in terms of atomic movements came *after* the discovery of the neutron. Geoffrey Taylor (*1*) was the great name here, and Nabarro and I (*2*) first tried to explain why metallic alloys are hard. The years that passed before anyone tried to get a theoretical understanding of electrons in glass surprises me even more. After all, the striking fact about glass is that it is transparent, and that one does not have to use particularly pure materials to make it so. But, in terms of modern solid-state physics, what does transparent mean? It means that, in the energy spectrum of the electrons in the material, there is a gap of forbidden energies between the occupied states (the valence band) and the empty states (the conduction band); light quanta corresponding to a visible wavelength do not have the energy needed to make electrons jump across it. This gap is quite a sophisticated concept, entirely dependent on quantum mechanics, and introduced for solids in the 1930's by the pioneering work of F. Bloch, R. Peierls, and A. H. Wilson. The theory was based on the assumption that the material was crystalline. The gap, in most treatments, was closely related to Bragg reflection of the electron waves by the crystal lattice and the mathematical analysis was based on the assumption of a perfect crystal. Glass, and amorphous materials generally, do not give a sharp Bragg reflection; it is curious, therefore, that no one much earlier than my co-workers and I (*3*) in Cambridge less than 10 years ago seems to have asked the question, "How can glass be transparent?"

Actually, our curiosity was stimulated by the investigation of the Leningrad school under Kolomiets (*4*) from 1950 onward of electrical rather than optical properties of the glassy semiconductors. These are black glasses, containing arsenic, tellurium, and other elements, and for them the band gap lies in the infrared. The gap is sufficiently small to ensure that at room temperature an electron can be excited across it. The Leningrad experiments showed, it seems to me, that the concepts of a conduction and a valence band could be applied to glasses and, more remarkably, that the gap, and hence the conductivity, did not depend sensitively on composition. This is related to the fact that oxide glasses are normally transparent and can only be colored, as in medieval stained glass, by the addition of transition metal atoms, where an inner shell produces its own absorption spectrum, depending little on the surroundings. These properties of glass are in sharp contrast with the behavior of crystals, where the whole of silicon technology depends on the fact that if, for instance, phosphorus with its five electrons is added, four form bonds but the fifth is very loosely bound. The discovery of this property of glasses certainly makes Kolomiets one of the fathers of the branch of science that I am describing, as were others in Eastern European countries, notably R. Grigorovici in Bucharest and J. Tauc in Prague. The explanation of the property in chemical terms (*5*) seems to be that in a glass each atom will have the right number of neighbors to enable *all* electrons to be taken up in bonds. There are important exceptions to this, mainly for deposited films, which I will come to, but in most glasses cooled from the melt it seems to be true.

This being so, what is the nature of the "conduction band" in amorphous materials? Is there necessarily a "tail" of states extending through the gap, as assumed in an early and important paper by Cohen *et al.* (*6*)? The fact that most glasses are transparent makes this unlikely. Clues came from another idea due to Ioffe and Regel (*7*) in Leningrad, namely that the mean free path cannot be shorter than the electron wavelength, and from the vastly important paper, "Absence of diffusion in certain random lattices," published by Anderson (*8*) in 1958 and described in his Nobel lecture this year. We now understand that in any noncrystalline system the lowest states in the conduction band are "localized" —that is, traps—and that on the energy scale there is a continuous range of such localized states leading from the bottom of the band up to a critical energy (*9*) E_c, called the mobility edge (*6*), where states become nonlocalized or extended. This is illustrated in Fig. 1, which shows the density of states. There is an extensive literature calculating the position of the mobility edge with various simple models (*10*), but it has not yet proved possible to do this for a "continuous random network" such as that postulated for SiO_2, As_2Se_3, amorphous Si, or any amorphous material where the coordination number remains the same as in the crystal. This problem is going to be quite a challenge for the theoreticians, but now we depend on experiments for the answer, particularly those in which electrons are injected into a noncrystalline material and their drift mobilities measured. What one expects is that at low

---

The author is Professor of Physics at the Cavendish Laboratory, University of Cambridge, Cambridge, England CB3 0HE. This article is the lecture he delivered in Stockholm, Sweden, on 8 December 1977 when he received the Nobel Prize in Physics, a prize which he shared with Dr. P. W. Anderson and Dr. J. H. Van Vleck. The article is published here with the permission of the Nobel Foundation and will also be included in the complete volume of *Les Prix Nobel en 1977*, as well as in the series Nobel Lectures (in English) published by the Elsevier Publishing Company, Amsterdam and New York. Dr. Van Vleck's lecture appeared in the 14 July issue, page 113, and Dr. Anderson's lecture in the 28 July issue, page 307.

0036-8075/78/0908-0871$01.25/0 Copyright © 1978 AAAS

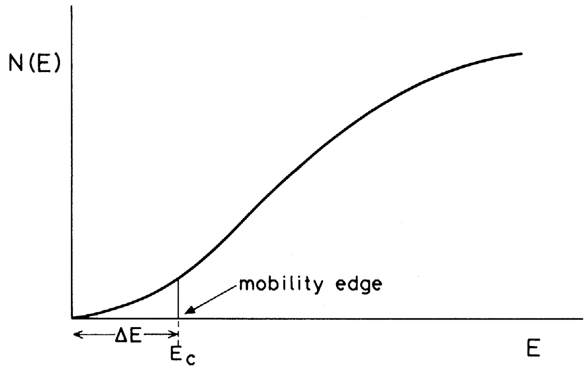


Fig. 1. Density of states in the conduction band of a noncrystalline material, showing the mobility edge E_c separated by an energy ΔE from the band edge.

temperatures charge transport is by "hopping" from one localized state to another, a process involving interaction with phonons and with only a small activation energy, while at high temperatures current is carried by electrons excited to the mobility edge, the mobility behaving as $\mu_0 \exp(-\Delta E/kT)$. With this model the drift mobility, conductivity, and thermopower are illustrated in Fig. 2 and [following a theory due to Friedman (*11*)] the Hall mobility can also be calculated. Owing to the brilliant work of Spear, Le Comber, and co-workers (*12*), it is clear that this is just what happens in at least one material, silicon deposited from SiH_4 in a glow discharge. As regards other materials, there is good evidence (*13*) that "holes" in arsenic telluride behave the same way, although there are other interpretations (*14*). But in other noncrystalline materials—notably for electrons in liquid rare gases (*15*), vitreous silicon dioxide (*16*), and some others—there is no evidence for a mobility edge at all, the drift mobility *decreasing* with increasing temperature. In some materials, then, the range of localized states (ΔE in Fig. 1) must be smaller than kT at room temperature. We await theoretical predictions of when this should be so.

For semiconductors, then, the data are rather scanty and we may ask how strong the evidence is for the existence of localized states and for a mobility edge generally for electrons in disordered systems. Apart from silicon deposited in a glow discharge, far and away the strongest evidence, in my view, comes from systems of the type which Anderson has called Fermi glasses. Here one must go back to the model of a metal introduced in the very early days of quantum mechanics by Sommerfeld. Electron states in a crystalline metal are occupied up to a limiting Fermi energy E_F, as in Fig. 3. The density of states at the Fermi level, which I denote by $N(E_F)$, determines the electronic specific heat and the Pauli paramagnetism. These statements remain true if the medium is noncrystalline, or if there is a random field of any kind as in an alloy; but in this case states at the bottom of the band, or possibly right through it, are localized. They may be localized at the Fermi energy. If so, we call the system a Fermi glass. Although the specific heat and Pauli magnetism behave as in a metal, the conductivity does not; it tends to zero with decreasing temperature.

Let us examine a system in which the density of electrons or degree of disorder can be varied, either by changing the composition or in some other way. Thus if the Fermi energy crosses the mobility edge, a "metal-insulator transition" occurs, of a kind which I have called an Anderson transition (*17*). I will now examine the electrical behavior of such a system. If E_F lies well above any mobility edge, we expect the behavior familiar in most liquid metals, and the conductivity can be treated by the theory put forward by Ziman (*18*) in 1961—one of the first successful approaches to conduction in noncrystalline materials—which showed that such problems were capable of exact treatment and encouraged the rest of us to try our hands. Ziman's theory is a "weak scattering" theory, the mean free path L being large compared with the distance between atoms a. As one increases the strength of the scattering, one reaches the Ioffe-Regel condition (in this case $L \sim a$), and the conductivity is then about

$$\frac{1}{3}e^2/\hbar a \sim 3000\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

if $a \sim 3$ angstroms. If the disorder gets stronger and stronger, Anderson localization sets in. The conductivity just before it occurs is then

$$\text{constant} \times e^2/\hbar a$$

where the constant depends on the Anderson localization criterion and is probably in the range 0.1 to 0.025. I have called this quantity the minimum metallic conductivity (*9*, *19*) and denoted it by $\sigma_{\min}$. For $a \sim 3$ Å it is in the range 250 to 1000 $\text{ohm}^{-1}\ \text{cm}^{-1}$, although in systems for which a is larger, such as impurity bands, it is smaller. I have maintained for several years that if the conductivity is finite in the limit of low temperatures, it cannot be less than this. This really does seem to be the case, and there is quite strong evidence for it, some of which I will describe. But the proposal proved very controversial (*20*) and only recently, through the numerical work of Licciardello and Thouless (*21*) and other analytical work, is it carrying conviction among most theorists.

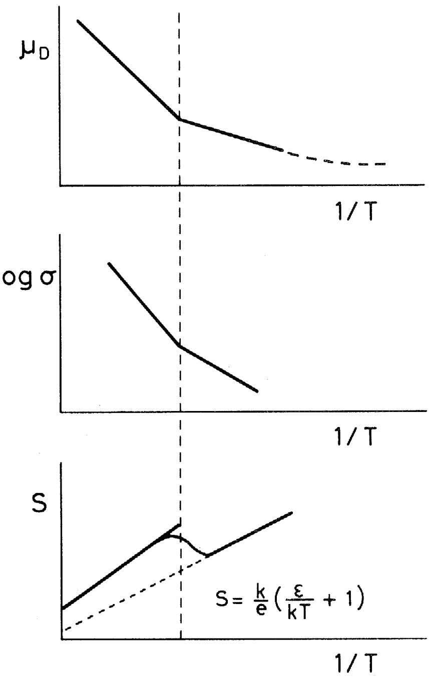


Fig. 2. Diagram showing schematically as functions of the reciprocal temperature the drift mobility μ_D, the conductivity σ, and the thermopower S of a material having a conduction band as in Fig. 1. The ϵ is equal to $E_c - E_F$.

Now let me ask what happens when the Fermi energy lies below the mobility edge, so that states at the Fermi energy are localized, and the material is what I called a Fermi glass. There are two mechanisms of conduction; at high temperatures electrons are excited to the mobility edge, so that

$$\sigma = \sigma_{\min} \exp[-(E_c - E_F)/kT] \qquad (1)$$

and at low temperatures conduction is by thermally activated hopping from one level to another. In 1969 I was able to show (*5*) that the latter process should give a conductivity following the law

$$\sigma = A \exp(-B/T^{1/4}) \qquad (2)$$

with B depending on the radial extension of the wave functions and the density of states. In two dimensions $T^{1/4}$ becomes

$T^{1/3}$. There has been quite a literature on this (*22*) following my elementary proof, and perhaps the effect of correlation is not yet perfectly understood, but I am convinced (*23*) that $T^{1/4}$ behavior is always to be expected in the limit of low temperatures.

It follows, then, that for a system in which one can vary the number of electrons, the plot of resistivity against $1/T$ will be as in Fig. 4. If there is a high density of electrons, and E_F lies above E_c, the conductivity should be nearly independent of temperature. As the density of electrons is lowered, the Fermi energy falls until it reaches E_c, and then $\sigma = \sigma_{min}$. If the density falls still further, states are localized, giving conduction by the two mechanisms of Eqs. 1 and 2 at high and low temperatures, respectively.

As regards the systems to which this concept can be applied, there are many. One is the alloy $La_{1-x}Sr_xVO_3$, which I owe to my colleagues (*24*) in Professor P. Hagenmuller's laboratory at Bordeaux. In these, a vanadium *d* band contains a number of electrons which varies with *x*, and thus with composition. But the simplest system is the MOSFET (metal oxide-silicon field-effect transistor) illustrated in Fig. 5. In this, *two-dimensional* conduction takes place in an inversion layer at the Si-SiO_2 interface, the "band bending" being illustrated in Fig. 6. The electron gas in the inversion layer is degenerate at helium temperatures, and the beauty of the system is that the density of electrons can be varied simply by changing the gate voltage. Disorder arises because the oxide contains random charges—capable of being controlled by the technology. The investigations of Pepper *et al.* (*25*) and Mott *et al.* (*17*) showed behavior confirming the pattern of Fig. 4 in every detail, and reasonable values of σ_{min} (expected to be 0.1 $e^2/\hbar$ in two dimensions).

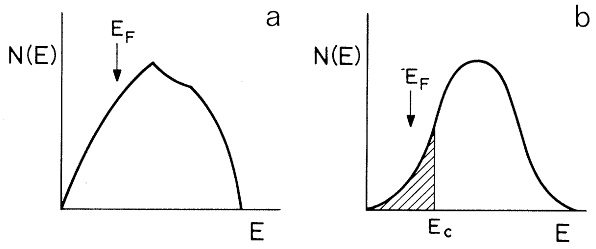
The $T^{1/4}$ behavior also occurs in many amorphous semiconductors such as silicon and germanium, and indeed was first observed in amorphous silicon by Walley (*26*), and the $T^{1/3}$ behavior was observed in thin films by Knotek *et al.* (*26a*). The Marburg group under Stuke (*27*) has investigated this phenomenon and its relation to electron spin resonance in detail. The idea here is that many amorphous materials contain "deep levels" due to defects such as dangling bonds; a photograph (Fig. 7) is included to show what is meant. Some of these may be charged and some not; if so, the density of states at the Fermi level is finite, and electrons can hop from one of these levels to another, giving a conductivity following Eq. 2.

Now I would like to finish the scientific part of this lecture by mentioning two new things and two old ones.

One of the new things is the important discovery by Spear and co-workers (*28*, *29*) that one *can* dope deposited films of silicon, for instance by depositing PH_3 with SiH_4. Much of the phosphorus seems to go in with three nearest neighbors, so that there are no loosely bound electrons, but sufficient phosphorus takes up fourfold coordination to give donors. These lose their electrons to states in the gap, but the Fermi energy can be shifted very near to the conduction or the valence bands. It is thus possible to make comparatively cheap *p-n* junctions, with important implications for the economics of solar cells.

The other new thing is the introduction of the "negative Hubbard *U*" by Anderson (*30*), and the application of the idea to specific defects by Street and Mott (*31*) and by Mott *et al.* (*32*), with subsequent development by Kastner *et al.* (*33*). It is supposed by the latter authors that there is a real difference in glasses between defects and fluctuations in density, each making specific contribution to the entropy (*34*).

We think the model is applicable to materials in which the top of the valence band consists of lone pair orbitals (*35*)—for instance, selenium *p* orbitals that do not take part in a bond. If so, we believe that "dangling bonds" as shown in Fig. 5 will *either* contain two electrons or none, and thus show no free spin and be positively or negatively charged. The repulsive energy (the Hubbard *U*) due to two electrons on one site is compensated because the positive center can form a



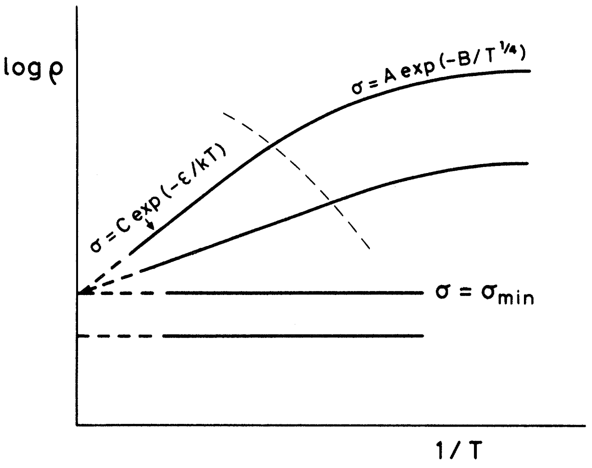
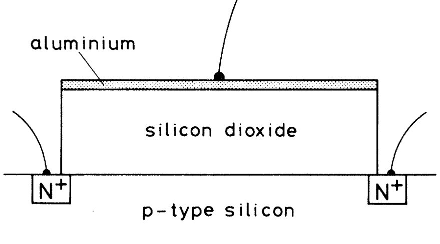


Fig. 3 (top). Density of states in a metallic conduction band, with states occupied up to a limiting Fermi energy E_F, (a) for a crystal, and (b) for an amorphous or liquid material, with localized states shaded and a mobility edge at E_c. Fig. 4 (bottom). Plot of log ρ (resistivity) against $1/T$ for a system in which the density of electrons can be altered so that ϵ (= $E_c - E_F$) changes sign, giving a metal-insulator transition of the Anderson type.



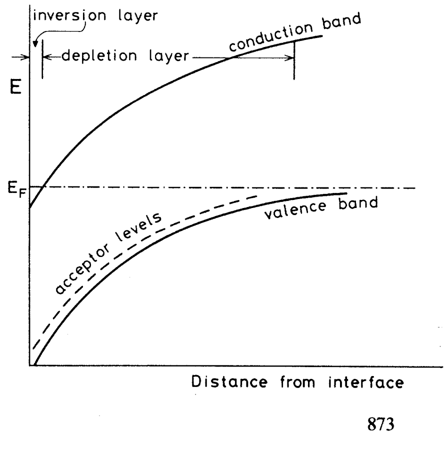


Fig. 5 (left). A MOSFET device for demonstrating two-dimensional conduction along the interface between *p*-type Si and SiO_2. Fig. 6 (right). Application of a field to the surface of a *p*-type semiconductor inducing an *n*-type surface layer.

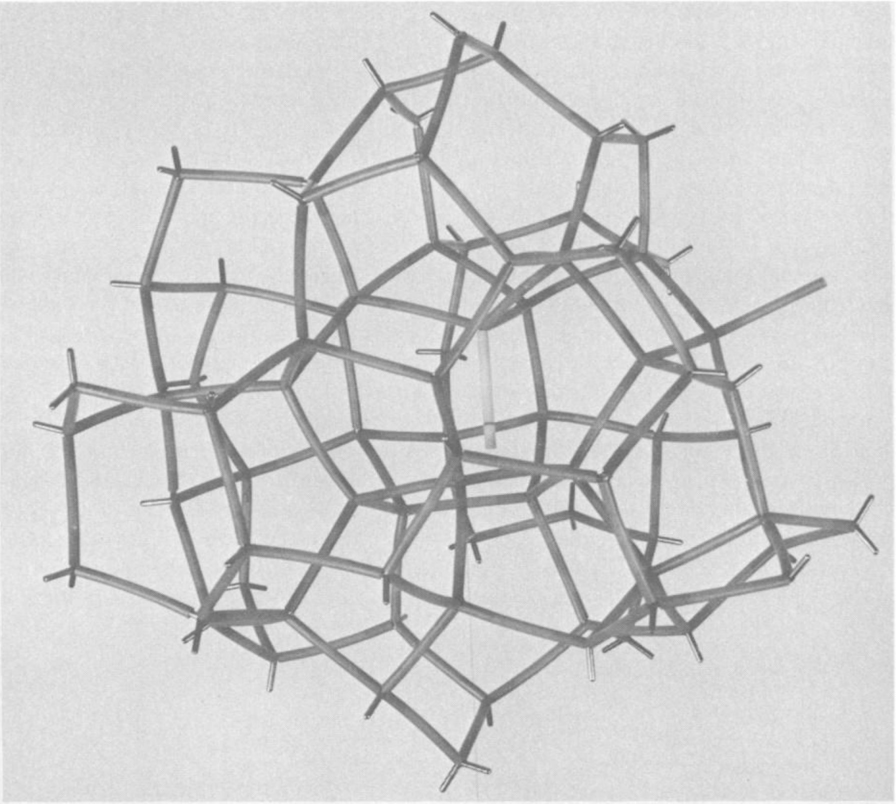


Fig. 7. A "dangling bond" in a continuous random network with fourfold coordination. [Courtesy of E. A. Davis]

strong bond if it moves toward another selenium, which is thus threefold coordinated. The positive and negative centers thus formed have been called by Kastner *et al.* (*33*) valence alternating pairs. The important point that these authors show is that one can form a pair without breaking a bond, while forming a neutral center (dangling bond) costs much more energy. The evidence that there are charged centers in these materials comes mainly from the experimental work of R. A. Street, T. M. Searle, and I. G. Austin on photoluminescence (*36*). We now think that the model is capable of explaining a great many of the properties of chalcogenide glasses, and perhaps of oxide glasses too. In particular, it shows how the Fermi energy can be held in position without introducing free spins, it seems capable of giving an explanation of dielectric loss, and it provides traps which limit the drift mobility. I feel that this work, particularly as formulated by Anderson, is another example of the Kolomiets principle that glasses cannot be doped; they form complete bonds whenever they can, even if the cost is negative and positive centers.

I said I would end by talking about two old things. One is the use of amorphous selenium for office copying by the Xerox company—a multibillion dollar industry developed, as is so often the case, before anybody had tried to make theories of the processes involved. When the subject became fashionable all over the world, we found, of course, that the Xerox scientists knew a great deal about it, and their recent contributions, particularly on dispersive transport (*37*), are of the highest importance.

The other comparatively old thing is the threshold switch invented by Ovshinsky (*38*). This in its simplest form consists of a deposited film of a chalcogenide glass about 1 micrometer thick, with a molybdenum or carbon electrode on each side. Such a system switches into a highly conducting state as the potential across it is increased, switching off again when the current through it drops below a certain value (Fig. 8). The claims made for this device generated a considerable amount of controversy, it being suggested that a thermal instability was involved and that similar phenomena had been observed many years ago. I do not think this is so, and in 1969, soon after the phenomenon was brought to my notice, I proposed (*39*) that it is an example of double injection, holes coming in at one electrode and electrons at the other. This is still my opinion. Experimental work, notably by Petersen and Adler (*40*) and by Henisch and Pryor (*41*), makes it practically certain that the conducting channel is not hot enough to appreciably affect the conductivity. The work of Petersen and Adler shows that in the on-state the current flows in a channel in which the density of electrons and holes and the current density do not depend on the total current; as the current increases, the channel simply gets wider, and can be much thicker than the thickness of the film. My own belief (*42*) is that the channel has strong similarities to the electron-hole droplets in crystalline germanium, that even at room temperature one has to do with a *degenerate* plasma of electrons and holes, and that the density of carriers is such that the Fermi energies of both gases lie above the respective mobility edges; only thus can the observed mobilities (~ 1 cm^2/V-sec) be explained. But we are still far from a full understanding of the behavior of this fascinating device.

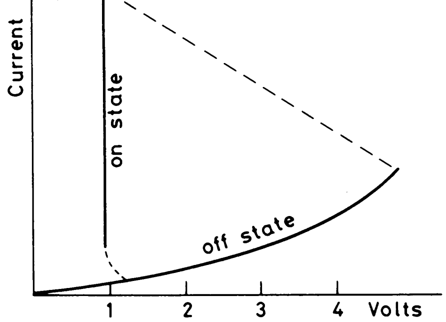


Fig. 8. Current-voltage curve of a threshold switch consisting of a thin chalcogenide film between two electrodes.

Finally, since I think that mine is the first Nobel prize to be awarded wholly for work on amorphous materials, I would like to say that I hope this will give a certain status to a new, expanding, and at times controversial subject. The credit for the prize must certainly be shared with people with whom I have talked and corresponded all over the world. I myself am neither an experimentalist nor a real mathematician; my theory stops at the Schrödinger equation. What I have done in this subject is to look at all the evidence, do calculations on the back of an envelope, and say to the theoreticians, "If you apply your techniques to this problem, this is how it will come out," and to the experimentalists just the same thing. This is what I did for $T^{1/4}$ hopping and the minimum metallic conductivity. But without these others on both sides of the fence I would have got nowhere. My thanks are due particularly to my close collaborator Ted Davis, joint author of our book on the subject (*43*), to Walter Spear and Mike Pepper in the U.K., to Josef Stuke in Marburg, to Karl Berggren in Sweden, to Hiroshi Kamimura in Japan, to Mike Pollak, Hellmut Fritzsche, and many others in the United States, and of course to Phil Anderson.

References and Notes

→ G. I. Taylor, *Proc. R. Soc. London Ser. A* **145**, 362 (1934).
2. N. F. Mott and F. R. N. Nabarro, *Proc. Phys. Soc. London* **52**, 86 (1940); *Report on Strength of Solids* (Physical Society, London, 1940), p. 1.
3. See papers in N. F. Mott, Ed., *Amorphous and Liquid Semiconductors* (North-Holland, Amsterdam, 1970).
4. For a review, see B. T. Kolomiets, *Phys. Status Solidi* **7**, 359 (1964).
5. N. F. Mott, *Philos. Mag.* **19**, 835 (1969).
6. M. H. Cohen, H. Fritzsche, S. R. Ovshinsky, *Phys. Rev. Lett.* **22**, 1065 (1969).
7. A. F. Ioffe and A. R. Regel, *Prog. Semicond.* **4**, 237 (1960).
8. P. W. Anderson, *Phys. Rev.* **109**, 1492 (1958).
9. N. F. Mott, *Adv. Phys.* **16**, 49 (1967).
10. J. T. Edwards and D. J. Thouless, *J. Phys. C* **5**, 807 (1972).
11. L. Friedman, *J. Non-Cryst. Solids* **6**, 329 (1971).
12. W. E. Spear, *Adv. Phys.* **23**, 523 (1974).
13. P. Nagels, R. Callaerts, M. Denayer, in *Amorphous and Liquid Semiconductors*, J. Stuke and W. Brenig, Eds. (Taylor & Francis, London, 1974), p. 867.
14. D. Emin, C. H. Seager, R. K. Quinn, *Phys. Rev. Lett.* **28**, 813 (1972).
15. L. S. Miller, S. Howe, W. E. Spear, *Phys. Rev.* **166**, 871 (1968).
16. R. C. Hughes, *Phys. Rev. Lett.* **30**, 1333 (1973); *Appl. Phys. Lett.* **26**, 436 (1975); *Phys. Rev. B* **15**, 2012 (1977).
→ N. F. Mott, M. Pepper, S. Pollitt, R. H. Wallis, C. J. Adkins, *Proc. R. Soc. London Ser. A* **345**, 169 (1975).
18. J. M. Ziman, *Philos. Mag.* **6**, 1013 (1961).
19. N. F. Mott, *ibid.* **26**, 1015 (1972).
20. M. H. Cohen and J. Jortner, *Phys. Rev. Lett.* **30**, 699 (1973).
21. D. C. Licciardello and D. J. Thouless, *J. Phys. C* **8**, 4157 (1975).
22. B. I. Shklovskii and A. L. Éfros, *Sov. Phys. JETP* **33**, 468 (1971); V. Ambegaokar, B. I. Halperin, J. S. Langer, *Phys. Rev. B* **4**, 2612 (1971); M. Pollak, *J. Non-Cryst. Solids* **11**, 1 (1972).
23. N. F. Mott, *Philos. Mag.* **34**, 643 (1976).
24. P. Dougier and A. Casalot, *J. Solid State Chem.* **2**, 396 (1970).
25. M. Pepper, S. Pollitt, C. J. Adkins, R. E. Oakley, *Phys. Lett. A* **47**, 71 (1974).
26. P. A. Walley, *Thin Solid Films* **2**, 327 (1968).
26a. M. L. Knotek, M. Pollak, T. M. Donovan, H. Kurzman, *Phys. Rev. Lett.* **30**, 853 (1973).
27. J. Stuke, in *Amorphous and Liquid Semiconductors*, B. T. Kolomiets, Ed. (Nauka, Moscow, 1975), p. 193.
28. W. E. Spear and P. G. Le Comber, *Solid State Commun.* **17**, 1193 (1975).
29. W. E. Spear, *Adv. Phys.*, in press.
30. P. W. Anderson, *Phys. Rev. Lett.* **34**, 953 (1975).
31. R. A. Street and N. F. Mott, *ibid.* **35**, 1293 (1975).
32. N. F. Mott, E. A. Davis, R. A. Street, *Philos. Mag.* **32**, 961 (1975).
33. M. Kastner, D. Adler, H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976).
34. R. J. Bell and P. Dean, *Phys. Chem. Glasses* **9**, 125 (1968).
35. M. Kastner, *Phys. Rev. Lett.* **28**, 355 (1972).
36. For a review, see R. A. Street, *Adv. Phys.* **25**, 397 (1976).
37. H. Scher and E. W. Montroll, *Phys. Rev. B* **12**, 2455 (1975).
38. S. R. Ovshinsky, *Phys. Rev. Lett.* **21**, 1450 (1968).
39. N. F. Mott, *Contemp. Phys.* **10**, 125 (1969).
40. K. E. Petersen and D. Adler, *J. Appl. Phys.* **47**, 256 (1976).
41. H. K. Henisch and R. W. Pryor, *Solid State Electron.* **14**, 765 (1971).
42. D. Adler, H. K. Henisch, N. F. Mott, *Rev. Mod. Phys.*, in press.
43. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford Univ. Press, Oxford, ed. 1, 1971; ed. 2, 1978).

The Biology of Oxygen Radicals

The superoxide radical is an agent of oxygen toxicity; superoxide dismutases provide an important defense.

Irwin Fridovich

The aerobic life-style offers great advantages, but is fraught with danger. Complete reduction of a molecule of oxygen to water requires four electrons, and in a sequential univalent process several intermediates will be encountered. These are the superoxide anion radical, hydrogen peroxide, and the hydroxyl radical, and they are too reactive (*1*) to be well tolerated within living systems. Nevertheless, the univalent pathway of oxygen reduction does occur and these dangerously reactive intermediates must somehow be accommodated. The primary defense is provided by enzymes that catalytically scavenge the intermediates of oxygen reduction. The superoxide radical is eliminated by superoxide dismutases, which catalyze its conversion to hydrogen peroxide plus oxygen (*2*), and hydrogen peroxide is removed by catalases (*3*), which convert it to water plus oxygen, and by peroxidases (*4*), which reduce it to water, using a variety of reductants available to the cell. Figure 1 illustrates the univalent pathway of oxygen reduction and the catalytic scavenging of intermediates. It is clear that efficient removal of the first two intermediates of oxygen reduction, O_2^- and H_2O_2, will prevent formation of the third, $OH\cdot$. This is fortunate, since the hydroxyl radical reacts avidly with many substances (*5*) and its specific enzymatic scavenging would be impossible.

Multiple Defenses

Molecular oxygen, now so abundant in our atmosphere, is the product of photosynthesis. Blue-green algae are the most primitive organisms capable of true photosynthesis, in which light energy is used to derive reducing power from water, with the evolution of molecular oxygen (*6, 7*). Blue-green algae are not the simplest of organisms and they must have been preceded by many other life-forms. The appearance of the first blue-green algae, approximately 2×10^9 years ago (*8*), and the subsequent oxygenation of the biosphere imposed a stringent evolutionary pressure on the many organisms that, up to then, had lived and evolved in an anaerobic world. While evolving mechanisms for the utilization of oxygen, they had to develop defenses against its toxicity. Considering the situation of a common evolutionary pressure applied to a varied biota, it is not surprising that multiple defenses arose and have persisted.

At present there are superoxide dismutases with either iron or manganese at the active site, and still others with both copper and zinc (*2*). There are catalases that are hemoproteins (*3*), and others, found in organisms incapable of heme synthesis, that may be flavoproteins (*9*). There are heme-containing peroxidases (*4*) that can utilize a wide variety of electron donors for the reduction of H_2O_2, and others that contain selenium and specifically utilize reduced glutathione as the reducing substrate (*10*). The biological production of hydrogen peroxide and the existence of catalases and peroxidases have been known for more than a century (*3*). In contrast, the corresponding production of superoxide radical and the existence of superoxide dismutases have been appreciated for approximately one decade. I will devote the remainder of this article to recent findings in this newer field of investigation.

The author is James B. Duke Professor of Biochemistry at Duke University Medical Center, Durham, North Carolina 27710.

0036-8075/78/0908-0875$01.25/0 Copyright © 1978 AAAS