ELECTRONS IN GLASS

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by
NEVILL MOTT
Cavendish Laboratory, Cambridge, England

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 (2) and I 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 wave-length 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 Bloch, 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 coworkers and I (3) in Cambridge less than ten 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 onwards of electrical rather than the 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 infra-red. 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 coloured, 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 behaviour 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 Grigorovici in Bucurest and Tauc in Prague. The explanation in chemical terms (5) of this property seems to be that in a glass each atom will have the right number of neighbours 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, Fritzsche and Ovshinsky (6)? The fact that most glasses are transparent makes this unlikely. Clues came from another Leningrad idea due to Ioffe and Regel (7), namely that the mean free path cannot be shorter than the electron wavelength, and from the vastly important paper published by Anderson (8) in 1958, "Absence of diffusion in certain random lattices", described in his Nobel lecture this year.
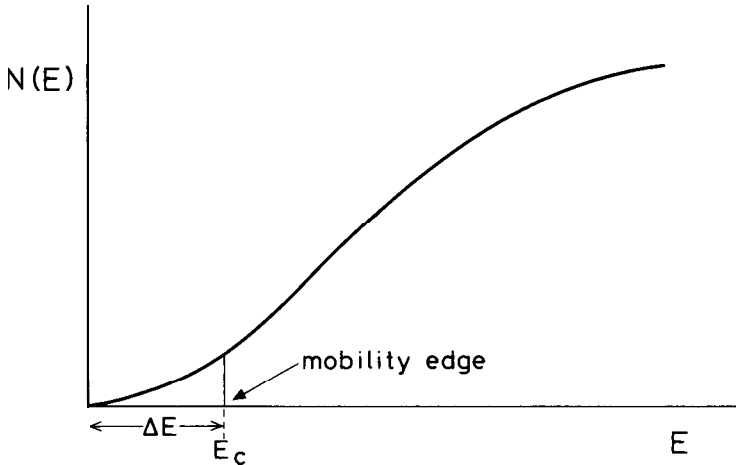

Fig. 1. The density of states in the conduction band of a non-crystalline material, showing the mobility edge E_c separated by an energy $\triangle E$ from the band edge.

We now understand that in any non-crystalline system the lowest states in the conduction band are "localized", that is to say 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 non-localized 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 co-ordination number remains the same as in the crystal. This problem is going to be quite a challenge for the theoreticians - but up till now we depend on experiments for the answer, particularly those in which

electrons are injected into a non-crystalline material and their drift mobilities measured. What one expects is that at low temperatures charge transport is by "hopping" from one localized state to another, a process involving inter-action 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 (12) and co-workers it is clear that this is just what happens in at least one material, silicon deposited from SiH₄ in a glow-discharge. As regards other materials, there is good evidence (13) that "holes" in arsenic telluride behave the same way, though there are other
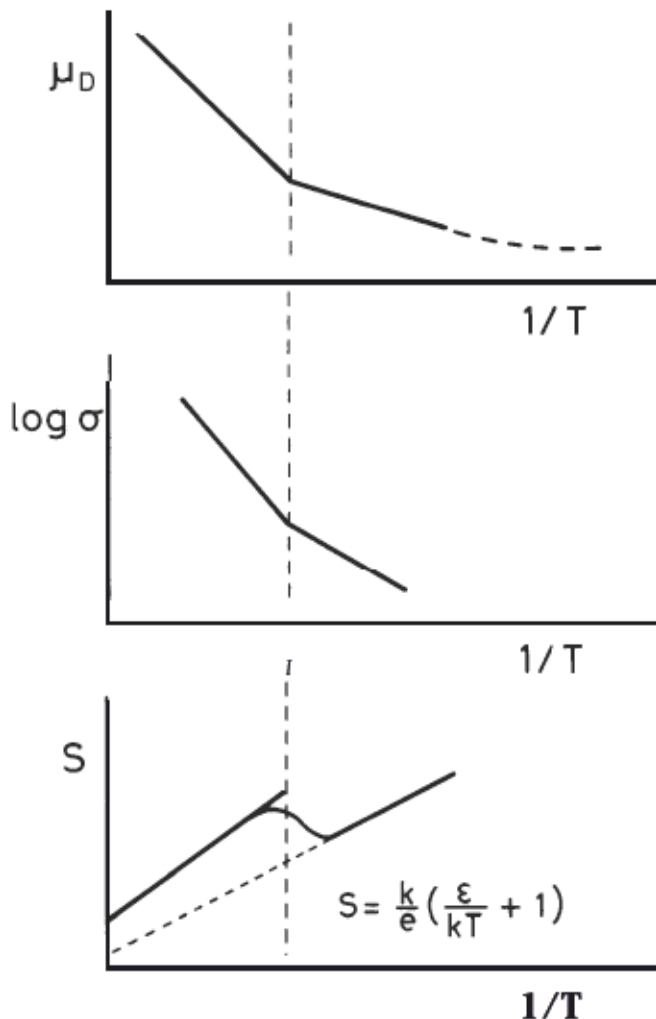

Fig. 2. The diagram shows schematically as functions of the reciprocal temperature the drift mobility μ_D, the conductivity σ and thermopower S of a material where the conduction band is as in fig. 1. ε is equal to E_c-E_F .

interpretations (14). But in other non-crystalline materials, notably for elec-
trons 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 (*AE* 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 is the evidence for the existence of localized states and for a mobility
edge generally for electrons in disordered systems? Apart from glow-dis-
charge deposited silicon, 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 non-crystalline, 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 mag-
netism behave as in a metal, the conductivity does not: it tends to zero with
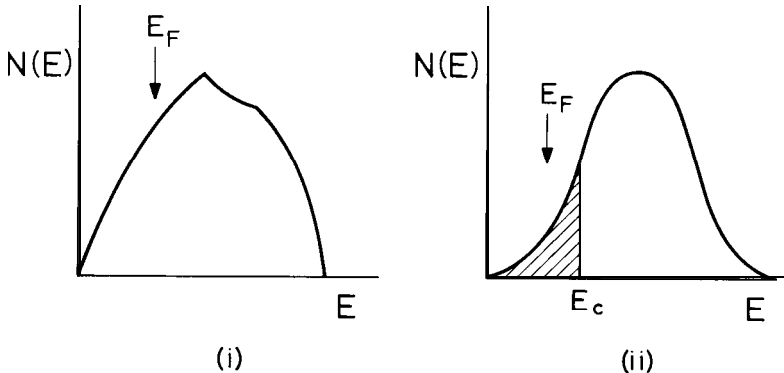decreasing   temperature.

Fig. 3. Density of states in a metallic conduction band, with states occupied up to a limiting
Fermi energy E_F. (i) is for a crystal, (ii) for an amorphous or liquid material, with localized
states shaded and a mobility edge at E_c.

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 behaviour of such a system. If the Fermi
energy E_F lies well above any mobility edge, we expect the behaviour 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 non-crystalline 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

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

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

$$\text{const} \ e^2/\hbar a,$$

where the constant depends on the Anderson localization criterion, and is probably in the range 0.1-0.025. I have called this quantity the "minimum metallic conductivity (9, 19) and denoted it by σ_{min}. For a $\sim$ 3 Å it is in the range 250-1000 Ω^{-1} cm^{-1}, though 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 due to the numerical work of Licciardello and Thouless (21), and other analytical work is it carrying conviction among most theorists.

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

$$\sigma = \sigma_{min} \exp \left\{ -(E_c - E_F)/kT \right\}, \tag{1}$$

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

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

with B depending on the radial extension of the wave functions and the density of states. In two dimensions $T^{\frac{1}{4}}$ becomes $T^{\frac{1}{3}}$. 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 $T^{\frac{1}{4}}$ behaviour 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 till 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 (1) and (2) at high and low temperatures respectively.
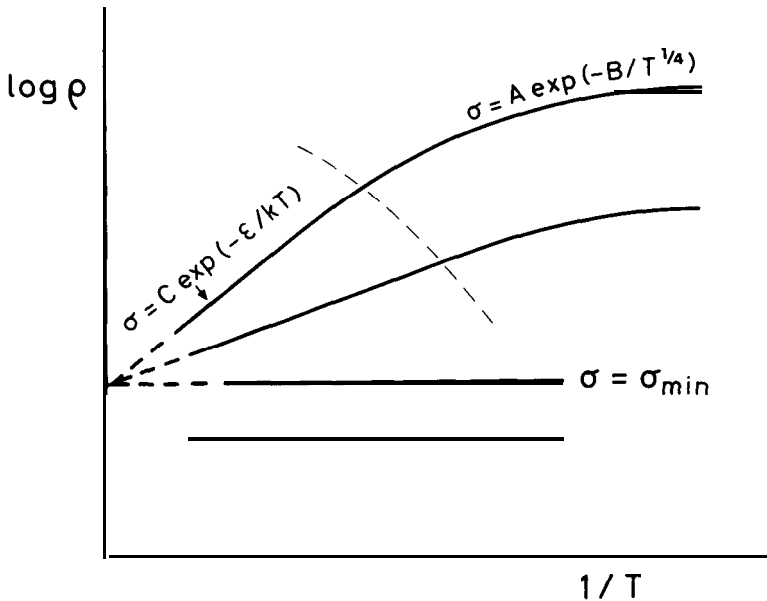
Fig. 4. Plot of log(resistivity) against l/T for a system in which the density of electrons can be altered so that ε (= E_c - E_F) changes sign, giving a metal-insulator transition of Anderson type.

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 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-SiO₂ interface, the "band bending" being illustrated
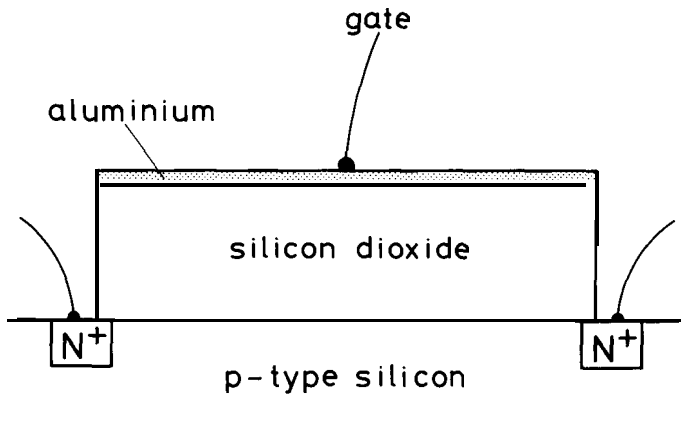

Fig. 5. A MOSFET device, for demonstration of two-dimensional conduction along the interface between the p-type Si and SiO₂.

in fig. 6. The electron gas in the inversion layers 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 and co-workers (25, 15) showed behaviour 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).
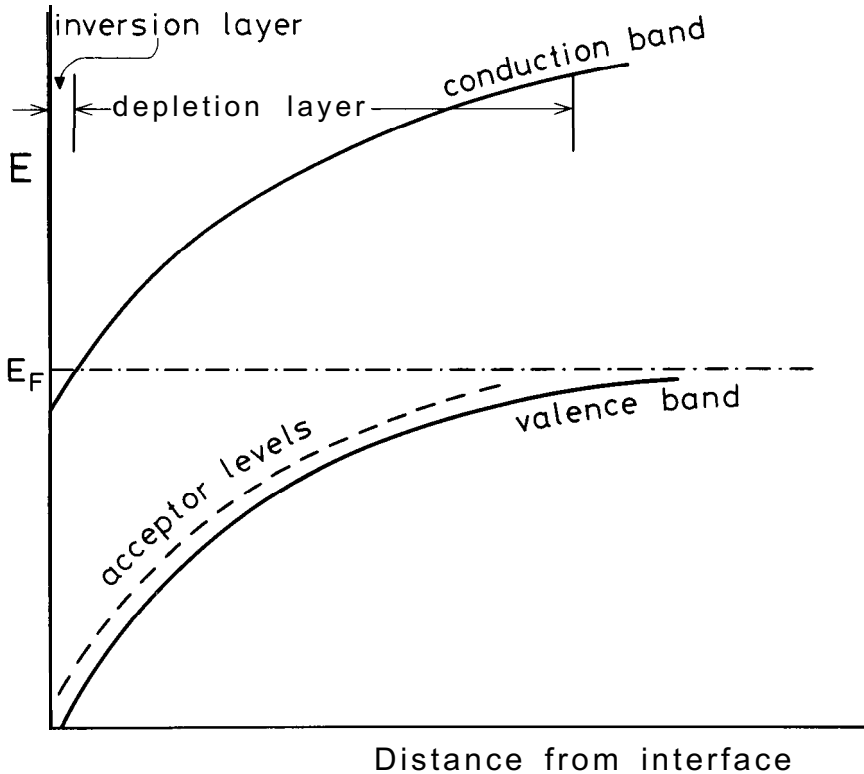

Fig. 6. Application of a field to the surface of a p-type semiconductor inducing an n-type surface layer.

$T^{\frac{1}{4}}$ behaviour occurs also in many amorphous semiconductors, such as Si and Ge, and indeed was first observed in amorphous silicon by Whalley (26) and $T^{\frac{1}{3}}$ in thin films by Knotek, Pollak et al (44). The Marburg group under Professor 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 hopping from one of these levels to another can occur, giving a conductivity following eqn (2).

Now I would like to finish the scientific part of this lecture by mentioning two new things and two old ones.
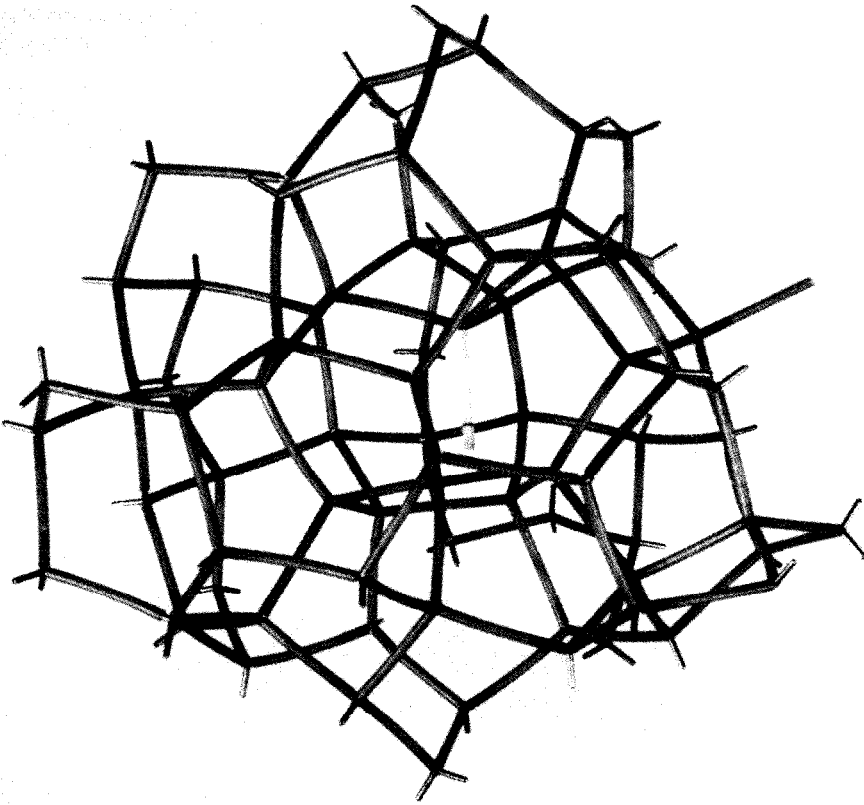
Fig. 7. A "dangling bond" in a continuous random network with fourfold co-ordination (courtesy of Dr E. A. Davis).

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 neighbours, so that there are no loosely bound electrons, but sufficient take up fourfold co-ordination so as 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, Davis and Street (32), with subsequent development by Kastner, Adler and Fritzsche (33). It is here supposed by the latter authors that there is a real difference in glasses between defects and fluctuations in density, each making their 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 in 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 centre can form a strong bond if it moves towards another selenium, which is thus threefold co-ordinated. The positive and negative centres thus formed have been called by Kastner et al "valence alternating pairs". The important point that these authors show is that one can form a pair without breaking a bond, while a neutral centre (dangling bond) costs much more energy to form it. The evidence that there are charged centres in these materials comes mainly from the experimental work of Street, Searle and Austin (36) on photoluminescence. 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 pinned 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 centres.

I said I would end by talking about two old things. One of course is the use of amorphous selenium for office copying by the Xerox company - a multi-billion 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 S. R. Ovshinsky (38). This in its simplest form consists of a deposited film of a chalcogenide glass about one micron 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 phenomenon had been observed many years ago. I do not think this is so, and proposed (39) in 1969, soon after the phenomenon was brought to my notice, that the phenomenon 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 (41), make it practically certain that the conducting channel is not hot enough appreciably to 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
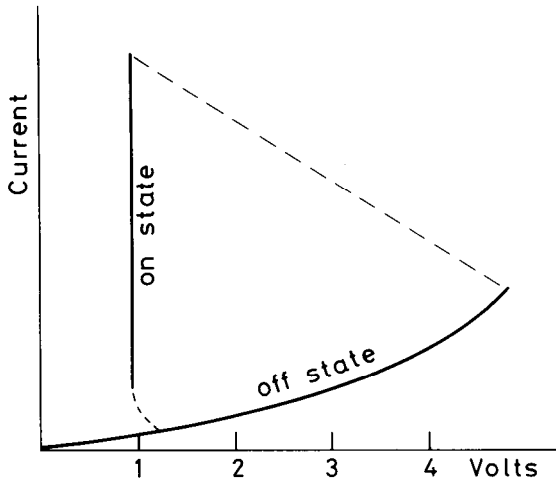
Fig. 8. Current voltage curve of a threshold switch, consisting of a thin chalcogenide film between two electrodes.

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 ($\sim 1 \text{ cm}^2/\text{V s}$) be explained. But we are still far from a full understanding of the behaviour of this fascinating device.

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've talked and corresponded all over the world. I myself am neither an experimentalist nor a real mathematician; my theory stops at Schrödinger equation. What I've done in this subject is to look at all the evidence, do calculations on the back of an envelope and say to the theoretician, "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 $T^{\frac{1}{4}}$ 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 to many others in the United States and of course to Phil Anderson.

REFERENCES

 1. Taylor, G. I., Proc. Roy. Soc. A 145, 362 (1934).
 2. Mott, N. F. and Nabarro, F. R. N., Proc. Phys. Soc. 52, 86 (1940) ; Report on Strength of Solids (The Physical Society, London) p. 1.
 3. See papers in Amorphous and Liquid Semiconductors (3rd International Conference), ed. N. F. Mott, North Holland, 1970.
 4. For a review, see B. T. Kolomiets, Phys. Stat. Solidi 7, 359 (1964).
 5. Mott, N. F., Phil. Mag., *19, 835* (1969).
 6. Cohen, M. H., Fritzsche, H. and Ovshinsky, S. R., Phys. Rev., Lett., 22, 1065 (1969).
 7. Ioffe, A. F. and Regel, A. R., Prog. Semicond., 4, 237 (1960).
 8. Anderson, P. W., Phys. Rev., *109,* 1492 (1958).
 9. Mott, N. F., Adv. Phys., *16, 49* (1967).
10. Edwards, J. T. and Thouless, D. J., J. Phys. C (Solid St. Phys.) 5, 807 (1972).
11. Friedman, L., J. Non-Cryst. Solids, 6, 329 (1971).
12. See review by W. E. Spear, Adv. Phys., 23, 523 (1974).
13. Nagels, P., Callaerts, R. and Denayer, M., Amorphous and Liquid Semiconductors (5th Int. Conf.), ed. J. Stuke and W. Brenig, Taylor & Francis, London, p. 867. (1974).
14. Emin, D., Seager, C. H. and Quinn, R. K., Phys. Rev. Lett., 28, 813 (1972).
15. Miller, L. S., Howe, S. and Spear, W. E., Phys. Rev., 166, 871 (1968).
16. Hughes, R. C., Phys. Rev. Lett., 30, 1333 (1973); Appl. Phys. Lett., 26, 436 (1975); Phys. Rev. B, *15,* 2012 (1977).
17. Mott, N. F., Pepper, M., Pollitt, S., Wallis, R. H. and Adkins, C. J., Proc. R. Soc. A, 345, 169 (1975).
18. Ziman, J. M., Phil. Mag., 6, 1013 (1961).
19. Mott, N. F., Phil. Mag., 26, 1015, (1972).
20. Cohen, M. H. and Jortner, J., Phys. Rev. Lett., 30, 699 (1973).
21. Licciardello, D. C. and Thouless, D. J., J. Phys. C: Solid St. Phys., 8, 4157, (1957).
22. Shklovskii, B. I. and Efros, A. L., Soviet Phys. JETP, 33, 468 (1971); V. Ambegaokar, B. I. Halperin and J. S. Langer, Phys. Rev. B, 4, 2612 (1971); M. Pollak, J. Non-Cryst. Solids, 11, 1 (1972).
23. Mott, N. F., Phil. Mag., 34, 643 (1976).
24. Dougier, P. and Casalot, A. J., Solid St. Chem., 2, 396 (1970).
25. Pepper, M., Pollitt, S., Adkins, C. J. and Oakley, R. E., Phys. Lett. A, 47, 71 (1974).
26. Walley, P. A., Thin Solid Films, 2, 327 (1968).
27. Stuke, J., 6th Int. Conference on Amorphous and Liquid Semiconductors, Leningrad, p. 193, ed. B. T. Kolomiets, Nauka.
28. Spear, W. E. and Le Comber, P. G., Solid St. Commun., 17, 1193 (1975).
29. Spear, W. E., Adv. Phys. 6, 811 (1977).
30. Anderson, P. W., Phys. Rev. Lett., 34, 953 (1975).
31. Street, R. A. and Mott, N. F., Phys. Rev. Lett., 35, 1293 (1975).
32. Mott, N. F., Davis, E. A. and Street, R. A., Phil. Mag., 32, 961 (1975).
33. Kastner, M., Adler, D. and Fritzsche, H., Phys. Rev. Lett., 37, 1504 (1976).
34. Bell, R. J. and Dean, P., Physics and Chemistry of Glasses, 9, 125 (1968).
35. Kastner, M., Phys. Rev. Lett., 28, 355 (1972).
36. For a review, see R. A. Street, Adv. Phys., 25, 397 (1976).
37. Scher, H. and Montroll, E. W., Phys. Rev. B, 12, 2455 (1975).
38. Ovshinsky, S. R., Phys. Rev. Lett., 21, 1450 (1968).
39. Mott, N. F., Contemporary Physics, 10, 125 (1969).
40. Petersen, K. E. and Adler, D., J. Appl. Phys., 47, 256 (1976).
41. Henisch, H. K. and Pryor, R. W., Solid-St. Electronics, 14, 765 (1971).
42. Adler, D., Henisch, H. K. and Mott, N. F., Rev. Mod. Phys. 50 (in press) 1978.
43. Mott, N. F. and Davis, E. A., Electronic Processes in Non-Crystalline Materials, Oxford University Press, 1st ed. 1971, 2nd ed. 1978.
44. Knotek, M. L., Pollak, M., Donovan, T. M. and Kurzman, H., Phys. Rev. Lett., 30, 853 (1973).