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Conduction and Switching in Non-crystalline Materials

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SUMMARY. The mechanism by which electrons move in crystalline semiconductors is now understood in some detail. The theoretical concepts necessary for the understanding of conductions in non-crystalline materials involve new ideas, which are discussed in this article. These include ' localized states ' and ' thermally activated hopping '. Some experiments designed to test the theory are described. Certain switching devices which make use of the electrical properties of non-crystalline materials are described, and theoretical explanations are suggested.

1. Introduction

The semiconductors used in transistors and most other electronic devices are crystalline. The theory of their behaviour has been developed in great detail in the last 20 years and the agreement with experiment is good. The study of non-crystalline semiconductors is much newer. These can be of various kinds; for instance, evaporated films of silicon and germanium are amorphous if the substrate on to which they are evaporated is cold enough. In addition, some kinds of glass are electronic semiconductors, particularly the so-called chalcogenide glasses of which As_3Se_2 is typical. By a 'glass' is meant a material which, when solidified from the melt, is non-crystalline. The conducting glasses such as As_3Se_2 are not transparent but absorb visible light. In other respects they are quite similar to the more familiar transparent glasses.

There are various reasons why conducting glasses and other non-crystalline semiconductors have recently attracted a good deal of attention. One is the theoretical interest of the problem. In crystalline substances, whether metals or semiconductors, wave-mechanics combined with a number of experimental techniques has given us very detailed knowledge of the behaviour of the electrons which carry the current. The concepts of a valence and conduction band, of a Fermi surface and of a wave-function with well defined wavelength, are all accepted and used wherever research is done. They all depend on the periodic nature of the crystal lattice in which the electron moves. The attempt to extend these concepts to the behaviour of electrons in glasses and other non-crystalline materials is new. The first quantitative success was the description given by Ziman (1961) of the conductivity of liquid metals. The treatment of semiconductors is more difficult; the absence of a crystalline arrangement of the atoms has a more profound effect and a new concept, that of localized wave-functions, appears. I shall explain what this means in this article.

The other reason for the interest in conducting glasses is that they can form the ' heart ' of a semiconducting switching device. Many industrial laboratories are investigating the possibilities. Two kinds of switches have been developed and are manufactured by Energy Conversion Devices Inc. of Detroit. Another kind has been described by Simmons and Verderber (1967). The mechanism by which they work is not fully understood; some suggestions are made in this article.

2. Conduction in non-crystalline materials

The theoretical concepts appropriate for the description of conduction in non-crystalline materials will now be described. In crystalline materials the band structure of the material is expressed through the density of states $N(E)$, the quantity $N(E)\mathrm{d}E$ representing the number of electron states with energy between E and $E+\mathrm{d}E$. The form of $N(E)$ is shown for a metal and for a semiconductor or insulator in fig. 1. In a metal the states are occupied by electrons up to a limiting energy E_{F} (the Fermi energy) ; in a semiconductor at the absolute zero of temperature a valence band is fully occupied and a conduction band empty. The wave-functions for the electrons are of the familiar form introduced by Bloch

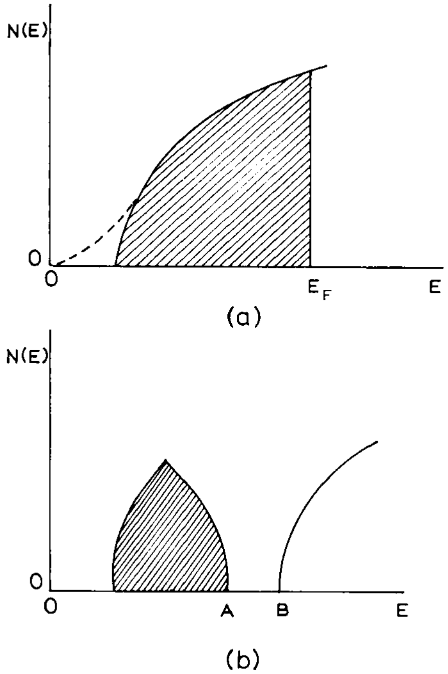

Fig. 1 (*a*) Density of states in a monovalent metal; the dotted line shown shows the change expected in a liquid. E_{F} is the Fermi energy. (*b*) Density of states in an intrinsic semiconductor; the occupied valence band is shaded. AB is the ' band gap '.

$$\psi(x)=\exp(ikx)\,u(x); \tag{1}$$

they are waves extending through the lattice modified by the field of the atoms (fig. 2). But of course even in a crystal the electrons are scattered by impurities and thermal vibrations of the atoms; a mean free path L can be defined and the wave-function (1) for an electron is only valid over a distance L. The approximation (1) is only useful if

$$kL \gg 1, \tag{2}$$

and thus if L is large compared with the wave-length $2\pi/k$. This is usually so in crystals.

Ziman's achievement in 1961 was to calculate the mean free path for electrons in liquid (or amorphous) metals. For most liquid metals the inequality (2) is still valid; so the effect of the atoms, while modifying the wave-function profoundly in the middle of each atom as in fig. 2, does not prevent propagation of the wave over quite a long distance. This means that ' perturbation theory ' is an appropriate mathematical method for the treatment of this problem; apart from the oscillations in the middle of each atom, the effect of atoms on the wave and on the density of states is quite small.

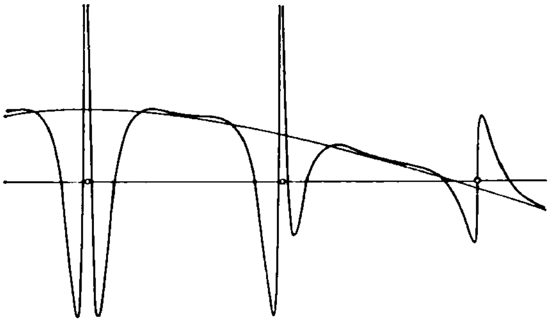

Fig. 2. Illustrating a Bloch wave-function modified by the field as in metallic sodium where it must behave like a 3s function near each atom (from Slater 1956).

For semiconductors, crystalline or non-crystalline, the effect of the lattice on the wave-functions and on the density of states is not small. In crystals it produces the energy gap of fig. 1. In non-crystalline materials an energy gap can certainly exist; otherwise ordinary optical glass and water would not be transparent. Mathematical treatment of the density of states in amorphous materials has proved extremely difficult, except when one uses one-dimensional models (for a review see Mott 1967, Halperin 1968); but one can say with reasonable certainty that in many such materials the gap either persists, as in glass (fig. 3 (*b*)), or is replaced by a minimum (fig. 3 (*a*)), which we shall call

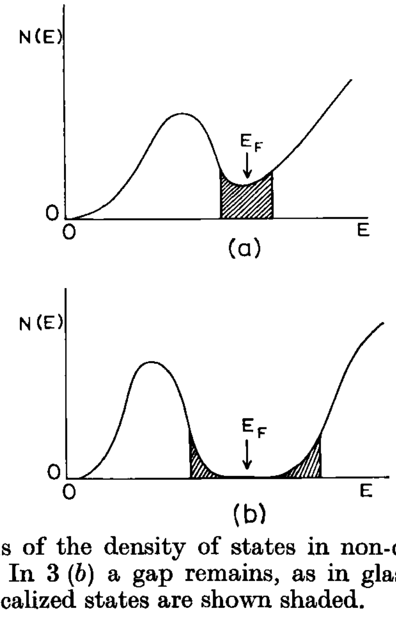

Fig. 3. Suggested forms of the density of states in non-crystalline insulators and semiconductors. In 3 (*b*) a gap remains, as in glass; in 3 (*a*) the gap has disappeared. Localized states are shown shaded.

a pseudogap. Such a pseudogap may exist in amorphous selenium or As_2Se_3 glasses. Near the extremities of the gap, or in the ' pseudogap ', the wave-functions are very strongly perturbed by the irregular arrangement of the atoms. If we describe the wave-functions by a function of the form shown in fig. 2, the direction of the electron will hardly remain constant for more than one interatomic distance; the electron will move by a sort of Brownian movement through the lattice, being deflected by every atom it passes through. The mean free path is of the order of the interatomic distance.

For energies in the pseudogap, or very near to the extremities of the conduction and valence bands, the wave-functions become localized; an electron in a localized state can be described as trapped, so this means that the absence of crystalline order produces a high density of traps. If trapped, an electron cannot move unless thermal energy frees it. The range of energies in which states are localized is shown shaded in fig. 3; if the Fermi energy lies in the shaded region, then at $T = 0$ the conductivity will vanish. At a finite temperature, each time the electron moves it gains or gives up energy from or to phonons. Such a process of conduction is called ' thermally activated hopping '. We denote by E_c the energy separating the range in which states are localized and the range in which they are not.

The idea of traps is of course familiar in crystalline semiconductors; impurities or defects give rise to electron states below the conduction band; an electron in a trap cannot get out unless it receives energy from some source. What is not so familiar is the idea that one can have a *continuum* of energy levels, as shown by the shaded area in fig. 3, and in each of these energy levels the electron is trapped and unable to move. Almost anyone when he looks at this conclusion for the first time is incredulous; he feels that, if there is a *continuum* of energy levels, the electron ought to be able to tunnel from one trap to another one which has exactly the same value of the quantized energy. The electron may have to go a long way to find another state with just the same energy, but an electron can tunnel any distance, so the conductivity will be finite. But this conclusion turns out to be wrong. The proof is quite subtle. The main point of the proof, which will not be discussed further here, is that if two states are close enough together for tunnelling, they split into two states which do not have the same energy (Mott 1968 a). What the theory suggests is that the mobility of an electron with energy E in the localized region of energies is of the form

$$\mu = \mu_0 \exp\{-W(E)/kT\}, \tag{3}$$

and $W(E)$ tends to zero at the energy E_c. If this is so, it would be of interest to prove it by experiment.

The best known example of ' hopping ' is impurity conduction in doped and compensated semiconductors. This is the predominating mechanism of conduction in germanium and silicon at helium temperatures (Mott and Twose 1961). It arises because the wave-functions of the trapped electrons in (say) the phosphorus atoms with which the material is doped overlap slightly, so that tunnelling is possible from one atom to another. If the levels all had the same energy, then one would expect a narrow band of energy levels to be formed, with width J determined by the overlap (figs. 4 and 5). It will be half full, because there is one electron per centre. Actually, however, it will not conduct;

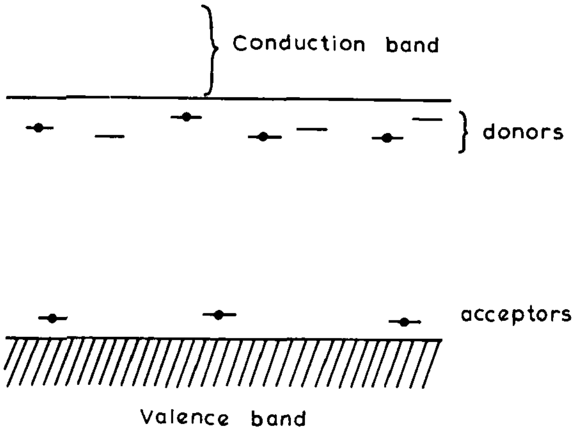

Fig. 4. Energy levels in a doped and compensated semiconductor. The dots represent an electron in a donor or acceptor.

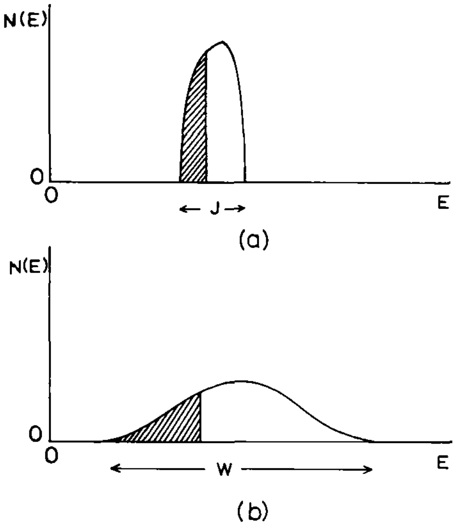

Fig. 5. Density of states and Fermi level in a doped and compensated semiconductor: (*a*) without broadening due to random fields; (*b*) with the actual broadening. Occupied states are shaded.

the Wilson model breaks down for narrow bands due to the electrostatic repulsion between the electrons, as first pointed out by the present author in 1949 (see also Mott 1961, 1968 b). But if the semiconductor contains some ‘ acceptors ’ (for example, gallium atoms) as well as the donors (for instance, phosphorus), then not all the donors will contain an electron; some will be lost to the acceptors. In this case we should expect metallic conduction, at any rate if the energies of the electrons in each donor centre were identical.

This is not what is observed. The plot of ρ against $1/T$ is shown in fig. 6, and it will be seen that unless the concentration is too high there is a well-marked activation energy, and the resistivity ρ shows every sign of tending to infinity as $T \rightarrow 0$. The explanation is the following. The acceptors each carry a negative charge, an electron having been transferred to each acceptor atom

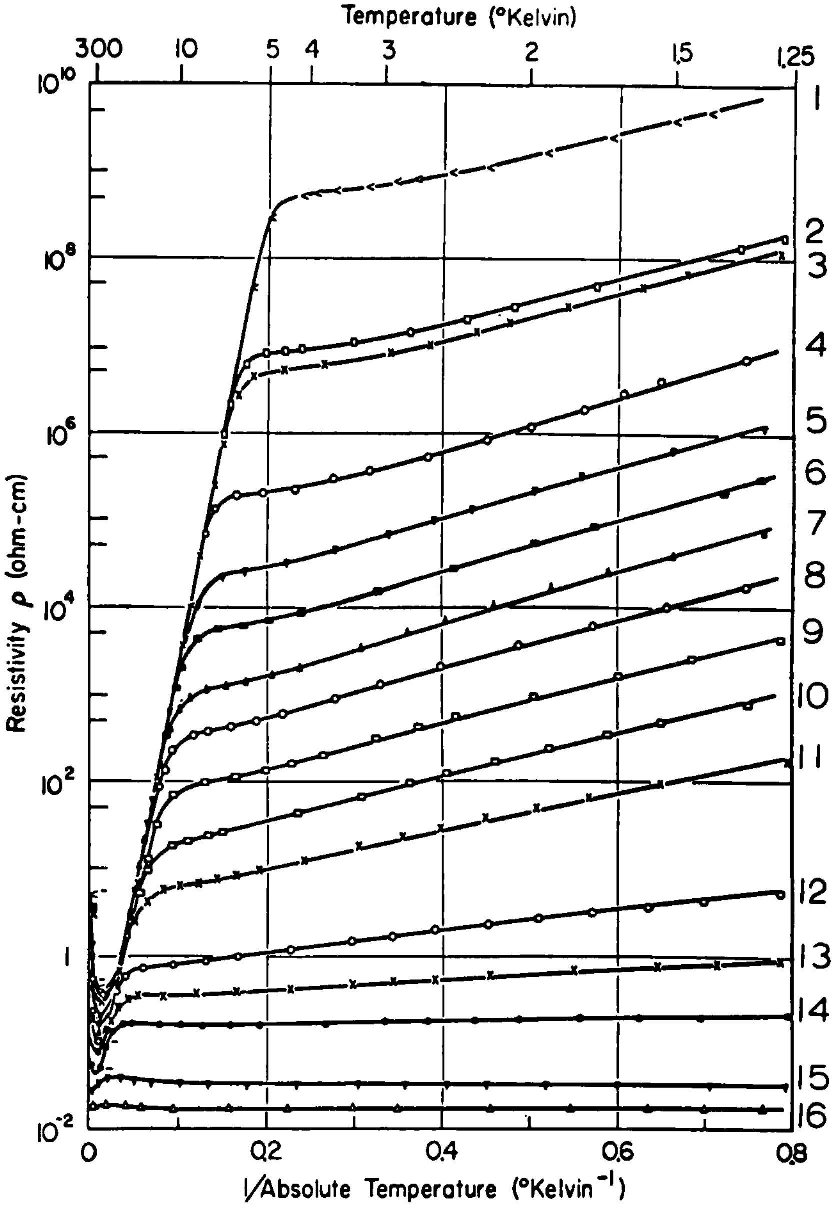

Fig. 6. Plot of the electrical resistance ρ of doped and compensated germanium against $1/T$, for different concentrations of the donors (Fritzsche and Cuevas 1960). The concentrations range from $7{\cdot}5 \times 10^{14}$ for specimen 1, $7{\cdot}13 \times 10^{16}$ for 12, 5×10^{17} for 15, all in centres per cm^3. The dopant was gallium.

from a donor. The acceptors are distributed in a quite random way in the germanium lattice. Therefore their charges produce an electric field which varies in a random way; and as a consequence the energy levels of donors are spread over a range of energies of order $W \sim e^2/\kappa R$, where κ is the dielectric constant and R the mean distance between acceptors. The band is therefore spread out as in fig. 5 (b)). And, if $W \gg J$, one would expect the mobility of an electron in the impurity band to be of type (2) because each time an electron jumps it gains or loses energy of order W, and the jumps in which it gains energy determine the mobility.

If W and J are at all comparable, we have to ask under what conditions we may expect thermally-activated hopping to occur, and under what conditions band behaviour with the mobility and conductivity remaining finite at very low temperatures. On this a well-known mathematical investigation by P. W. Anderson (1958) gives us the answer. His paper, entitled ' Absence of diffusion in certain random lattices ', is not easy reading, but it comes to the conclusion that if W/J is above a certain critical value, of order 5, there is no diffusion at $T=0$, which means that the states are localized.

In principle one can study the transition between hopping and band conduction by varying the concentrations of donors and acceptors, and some evidence that this occurs has been obtained (Mott and Davis 1968). However, an even more suitable system is provided by the compound cerium sulphide, investigated by Cutler and Leavy (1964) and interpreted by Cutler and Mott (1969). Cerium is trivalent; pure Ce_2S_3 is therefore an insulator. But it has the crystal structure of Ce_3S_4 ,the additional sulphur being included through the presence of randomly situated cerium vacancies. Therefore by adding cerium to Ce_2S_3 one adds electrons without introducing donors; one simply decreases the number of vacancies. The electrons may be thought of as moving in a highly disordered potential as in fig. 7 and with a density of states as in fig. 8. If our ideas are right there should be a range of energies in the conduction band in which states are localized ($E<E_c$) and a range in which

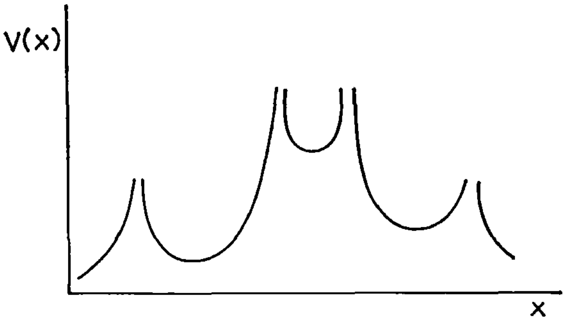

Fig. 7. Hypothetical potential energy of an electron in cerium sulphide (Cutler and Mott 1969).

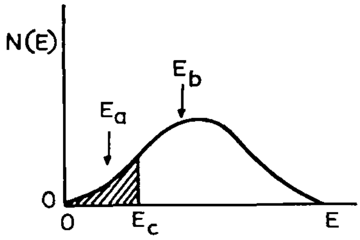

Fig. 8. Hypothetical density of states in cerium sulphide. The localized region is shaded. If the Fermi energy lies at E_a, conduction is by hopping; if at E_b, it is not.

they are not. Thus as the cerium content is increased and electrons added, the Fermi energy at $T=0$ will move from the localized to the non-localized range. At low temperatures the conductivity depends only on the behaviour of electrons near the Fermi energy. Therefore, for increasing concentrations of electrons, the resistance–temperature curves should look as in fig. 9.

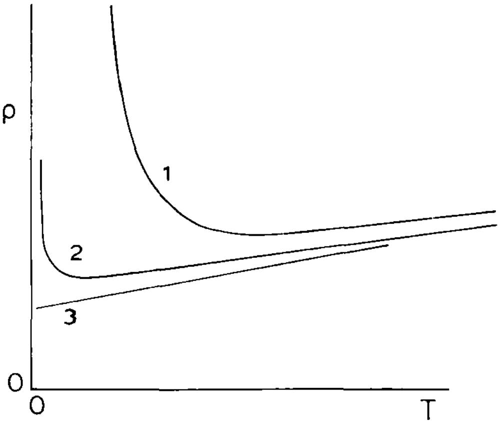

Fig. 9. Expected behaviour of the resistivity as a function of temperature in cerium sulphide. Curves 1, 2, 3 are for increasing concentration of electrons.

If—as some theoretical workers have suggested—the conductivity at $T=0$ does not vanish for any value of the energy, but merely tends towards zero as the energy is lowered, the resistance–temperature curves should be as in fig. 10. The actual observations of Cutler and Leavy are in fig. 11. They are not at present sufficient to distinguish between the two possibilities, but further development of this work doubtless will.

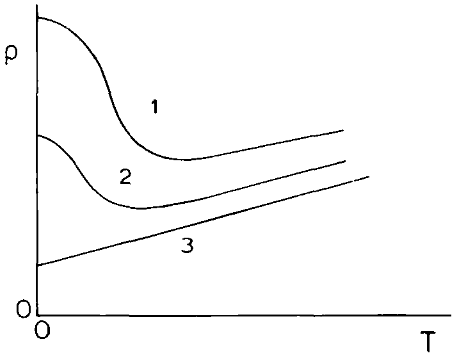

Fig. 10. Shows the expected behaviour according to another hypothesis, which we expect to be wrong.

Investigations have recently been carried out in the Cavendish Laboratory to see what happens when the Fermi energy lies in the pseudogap of fig. 3 (*b*) (Ferrier and Herrell 1969). The material chosen was the alloy system Mg–Bi; in the crystalline state it forms an intermetallic compound with the composition Mg_3Bi_2 and with a forbidden gap between valence and conduction bands; in the liquid there is a sharp minimum in the conductivity at that composition.

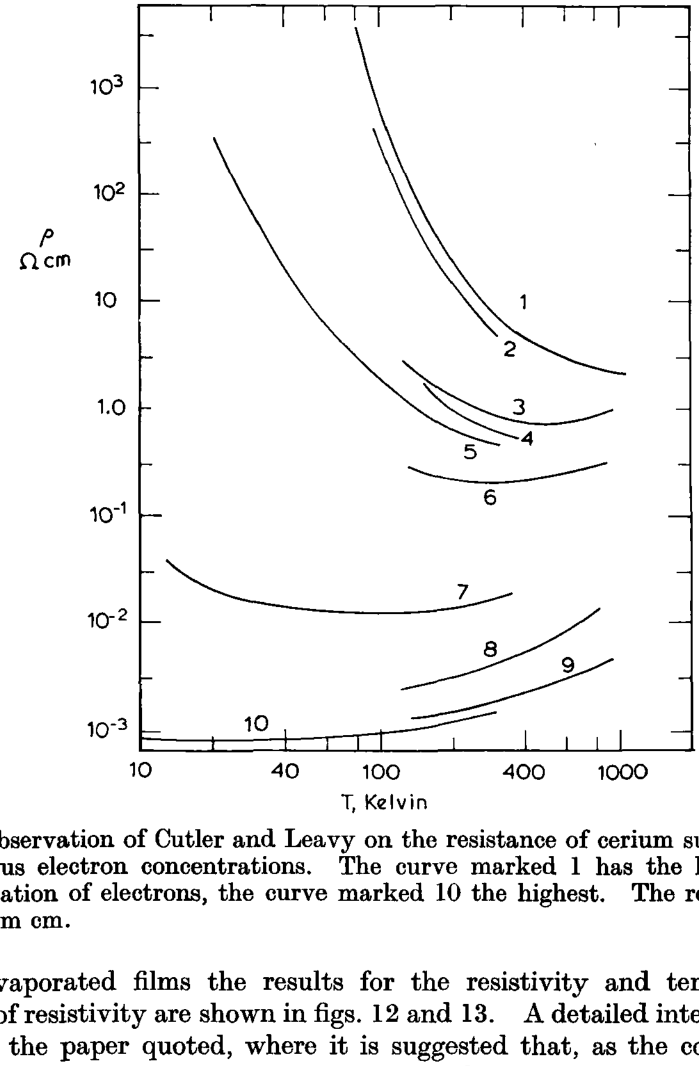

Fig. 11. Observation of Cutler and Leavy on the resistance of cerium sulphide, for various electron concentrations. The curve marked 1 has the lowest concentration of electrons, the curve marked 10 the highest. The resistivity is in ohm cm.

For the evaporated films the results for the resistivity and temperature-coefficient of resistivity are shown in figs. 12 and 13. A detailed interpretation is given in the paper quoted, where it is suggested that, as the composition changes, the Fermi energy moves across the pseudogap. Near the composition Mg_3Bi_2 the conductivity is by hopping, giving a low value and an increase of conductivity with temperature. For compositions some way from that of Mg_3Bi_2 it is thought that the Fermi energy lies in the region of energies where there is no localization, so the material behaves like an amorphous metal.

3. Switching devices

One of the most interesting applications of conduction in amorphous material is to switching devices in which a conducting glass is the heart of the device. A. H. Pearson of the Bell Telephone Laboratories reported in 1962 switching and memory effects in a glass belonging to the system As-Te-I; this was at the meeting of the Electrochemical Society in Los Angeles. These remarks were tape-recorded and published in *Advances in Glass Technology* (Plenum Press, New York, 1963). Eaton (1964) published the results of investigations of switching with these materials carried out at Corning Glass works. Kolomiets and Lebedev (1963) reported switching in a glass of the class TlAs $(Se, Te)_2$.

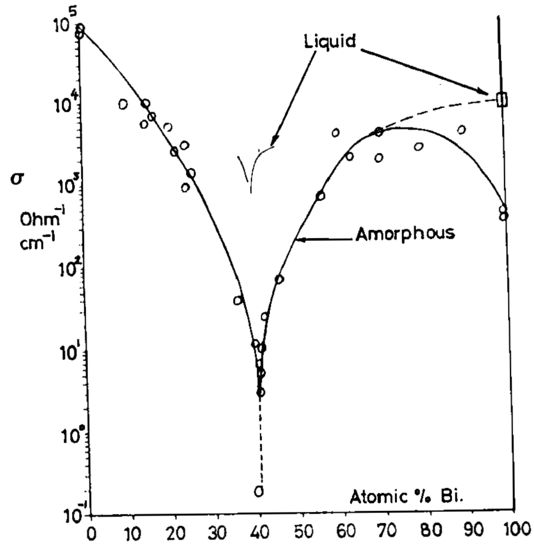

Fig. 12. Variation of conductivity of amorphous magnesium-bismuth films with composition (Ferrier and Herrell 1969).

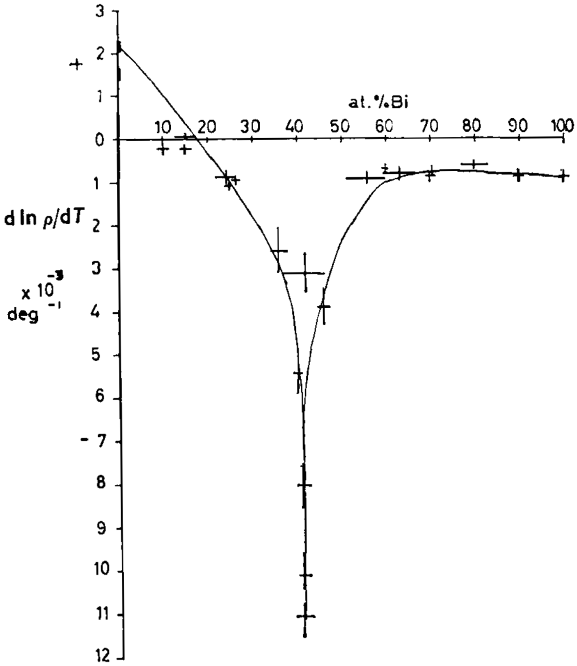

Fig. 13. Variation of the temperature coefficient of resistance with composition for amorphous magnesium-bismuth films (Ferrier and Herrell 1969).

Simmons and Verberder (1967) described a memory switch using amorphous silicon monoxide developed at the Standard Telecommunication Laboratories at Harlow. Switching in amorphous films of various semiconducting films has been observed by Chopra (1965). Ovshinsky (1968) has published some details of the Ovonic switch manufactured by his company based on evaporated films of a mixture of tellurium, arsenic, germanium and silicon, and there are many earlier references to them in the technical literature. These switches are of two types, the threshold switch and the memory switch. It is not at present clear what relationship, if any, they have to other switching mechanisms described in the literature, but the discussion of their properties at recent scientific conferences makes it possible to speculate with some confidence about the basic processes involved. Switching of the Ovshinsky type has been observed by Shaw (1969) in the author's laboratory in evaporated amorphous films of As_2Se_3.

The amorphous materials used are thought to be intrinsic semiconductors with a band gap E of ~ 1 eV, but smeared out as in fig. 3 (*a*)). There certainly exist localized states in the band gap, but apparently not enough to make a significant contribution to the conductivity; they are perhaps too far apart for tunnelling. But they do make a major contribution to the a.c. conductivity. Here according to Pollak and Geballe (1961) pairs of centres which are accidentally close together, so that electrons can tunnel fairly easily, give a term in the conductivity proportional roughly to the frequency. This is observed (Shaw 1969). But the d.c. current is normally carried by electrons or holes in the conduction or valence bands whose concentration is proportional to $\exp(-\frac{1}{2}E/kT)$, so that the room-temperature resistivity is high ($\sim 10^6$ ohm-cm).

An important point about glasses, unlike crystalline semiconductors, is that their conductivity is relatively insensitive to composition. In this they contrast strongly with crystalline semiconductors. It is thought that the structure arranges itself to take up all available electrons in bonds; thus phosphorus (valency 5) in crystalline germanium is surrounded by four germaniums, leaving one electron easily freed, while in the amorphous state it could be surrounded by five (fig. 14).

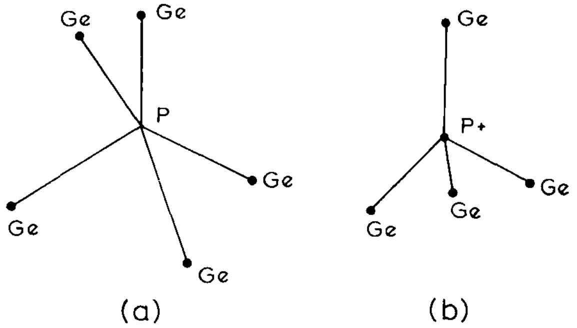

Fig. 14. Assumed surroundings of phosphorus (P) in amorphous germanium (*a*) contrasted with P+ in crystalline germanium (*b*).

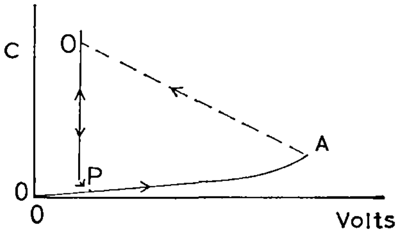

Fig. 15. Current-voltage curve for Ovonic switch.

The current-voltage behaviour of the Ovshinsky threshold switch is illustrated in fig. 15. At about 4 volts the current switches to the low resistance state, in which it remains as long as the current is not allowed to drop below the point P. If the current drops to a lower value, the material switches to the high resistance state. Switching times from A to O (fig. 15) are a fraction of a nanosecond.

More than one model has been proposed to explain why the device acts in this way. It seems likely that a conducting region $XX'YY'$ in fig. 16 is set up between the electrodes and that this shrinks and expands as the current varies along the line OP in fig. 15. The voltage across it remains constant. The author believes that in the high current state a Schottky barrier is set up at both boundaries (fig. 17). A ' Schottky barrier ' is the region where a very strong field exists in the neighbourhood of the contact between a semiconductor and metal, and must be due to a strong space charge in the semiconductor. If barriers of this type exist at both electrodes, and electrons and holes can tunnel through them, then electrons can be injected at A in fig. 17 and holes at B.

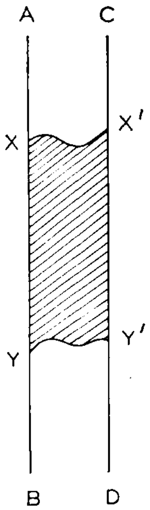

Fig. 16. To illustrate the behaviour of the Ovonic switch; AB, CD are the electrodes and the (shaded) low impedance region $XYY'X$ expands and shrinks as the current changes.

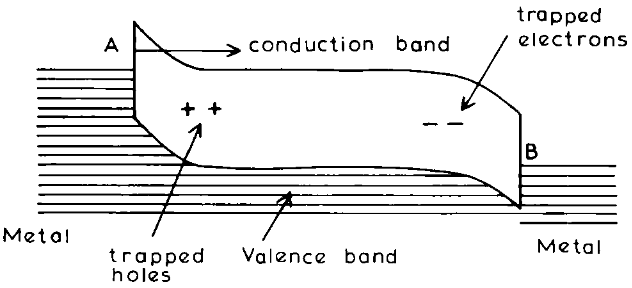

Fig. 17. Suggested form of conduction and valence bands in the low impedance state of a threshold switch. The curved lines show how the potential energy of a electron, at the top of the valence band or bottom of the conduction band, varies with position across the glass film, under the influence of the field produced by trapped electrons and holes.

In the high current state the resistance is almost independent of temperature, which certainly indicates that tunnelling is the factor determining the current; the hypothesis that carriers are injected at *both* electrodes is introduced because, if the barriers are to be maintained, holes must be trapped near the cathode and electrons near the anode. As already emphasized, an amorphous material is full of traps. Injected electrons and injected holes will frequently be trapped, and when they are they will eventually recombine. But near the cathode the electrons, which have just tunnelled through the barrier, are moving faster than in the body of the device and so do not combine so easily with positive holes. That is why a concentration of positive charge builds up there before the rate of recombination balances the rate of trapping. And the same is true of electrons near the anode.

The exact mechanism for switching from the high to the low impedance state is even more controversial. The present author thinks that as soon as the field is strong enough to give some strong-field emission from either electrode, trapping of carriers and the build-up of barriers will at once occur. But other mechanisms have been proposed at conferences and informal discussions.

Even more interesting is the ' memory ' or bistable switch. In this, once the device has switched to the 'on' or low impedance state it does not switch back when the voltage is removed. Switching times are of order 10^{-6} s. It may be switched back to the off-state by a high energy, short duration pulse. The switch described by Simmons and Verderber also has a memory in this sense. These switches therefore have the capacity to function as a memory element for binary notation with the advantage that they can be interrogated without destroying the present memory state.

As regards the mechanism, two hypotheses need examining. One is that the potential barriers of fig. 15 could be ' frozen in ' in some way. Certainly potential barriers which are apparently due to trapped electrons can be remarkably stable, as the work of Giaever (1968) on Josephson tunnelling through thin layers of CdS shows; the model of Simmons and Verderber, too, presupposes stability of trapped electrons. But for the Ovshinsky memory switches nobody has put forward a mechanism by which the trapped electrons could be stabilized and destabilized, and it seems certain that some rearrangement of the atoms of the glass is involved. A possible hypothesis is the following, which depends on the glass being a mixture of several components, or having composition some way from the exact chemical formula. In the glass as produced by evaporating a film in the first place, or after rapid cooling, all electrons are taken up in bonds, as in fig. 14 (*a*). Heating followed by very slow cooling would allow recrystallization, and, if the density of impurities with the wrong valency was high, one would obtain a material with the properties of a highly doped semiconductor. But it seems unlikely that in a switching device recrystallization occurs, even along narrow channels. It seems more likely that, while cooling from a high temperature results in a state where all electrons are taken up in bonds, cooling from a different temperature allows a rearrangement of the positions of atoms in which the strongest bonds (for instance, those characteristic of As_3Se_2) are formed, and other materials such as excess As or any of the other constituents present in a memory switch are left in positions where the outer electron cannot form a bond. The precise conditions of cooling to give the two states are under investigation.

In terms of semiconductor language, this would mean that in the low impedance state occupied states, or donors, are produced with energies in the band gap. The density of states in the band gap will thereby be increased. The experiments that we have quoted show that this will increase the conductivity; tunnelling from occupied to empty states will be easier, $W(E)$ in formula (3) becomes less and eventually an ' Anderson transition ' occurs and $W(E)$ disappears, as in cerium sulphide when the number of electrons is increased. The conductivity should then persist to low temperatures, as is observed down to 70°K for switches in the memory state.

Switching is thus due to rapid and slow cooling along a filament first formed by the threshold mechanism of fig. 16 through the material, the heating being produced by a current pulse.

All this is certainly speculative, and a good deal of further work will be essential before the behaviour of these materials is fully understood.

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