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# THERMAL SWITCHING IN METALS

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*Abstract:* A simple experiment with mercury showed that solid-liquid transition in metals may be utilized for a thermal formation of a current-voltage characteristic of N-type as well as for the switching from a state of lower to a state of higher resistance. As a measure for the switching effectiveness a factor $q$ appears, defined as a ratio of conductivities of the metal in liquid and solid state. The lower its magnitude the better are the switching characteristics. In pure metals $q$ is rather large but smaller values may be expected in alloys. Empirical rules governing design of such alloys are discussed.

## *1. Introduction*

Dealing with amorphous semiconductors Ovshinsky[1] discovered in 1968. a new effect in which electrical field causes a fast transition of a material from almost insulating to a highly-conductive state. The effect has drawn attention of many scientists and a great number of papers appeared in the years following Ovshinsky's discovery. They show that we are in fact faced with a variety of effects, now called by the common name — switching phenomena. The latest review of the field is given by Fritzsche[2].

For the purpose of this work it is not necessary to introduce the reader into the very intricate field of different kinds of switching effects and of mechanisms that govern them. It will be sufficient to describe two simple cases instead. In the first we will suppose a sample of a material whose electrical conductivity $\sigma$ increases in some fashion with temperature. At a definite temperature $T_c$ the supposed material undergoes a phase transition associated with a jump of conductivity to a higher value (Fig. 1 a.). The static current-voltage characteristic of the sample, due to non-isotropic self-heating coupled with subsequent phase transition, appears then to be of S-type[3] (Fig. 1 b.). The term »switching« denotes here the fast transition from point A to point B of the curve. It may be observed by measuring the sample characteristic in non-constant-current conditions. This type of switching is said to be of purely thermal nature since all possible electronic processes also able to form an S-curve were presumably excluded.

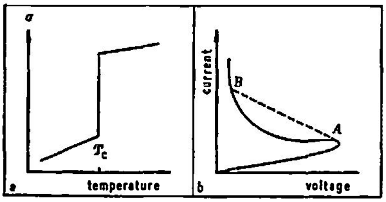


Fig. 1. $\sigma(T)$ and $I(V)$ characteristics of a material showing the switching of S-type.

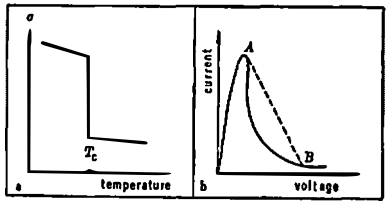


Fig. 2. $\sigma(T)$ and $I(V)$ characteristics of a material showing the switching of N-type.

In the second case our assumptions are reversed. Electrical conductivity of a material decreases with temperature and the phase transition at $T_c$ is associated with a jump of conductivity to a lower value (Fig. 2 a.). A purely thermal process leads then to the I—V characteristic of N-type[4] and to the switching from A to B in non-constant-voltage conditions (Fig. 2 b.). Note that the switching in two mentioned cases occurs in reversed directions.

Materials able to exhibit these effects belong much oftener to the first group than to the second. In fact, second group materials are relatively rare. Consequently the investigations to date were devoted predominantly to the S-type phenomena. However, N-type characteristics and the switching of this kind are of practical interest and therefore deserve a reasonable attention.

In this work the attention is confined to the metals. Their melting is in great many cases accompanied by a sharp decrease in electrical conductivity being thus a phase transition of the kind shown in Fig. 2 a. An N-type characteristic is possible and the extent of changes in current and voltage remains to be examined, i. e. it remains to be seen how effective can the switching be and what are its eventual side effects.

## 2. *Current-voltage characteristic of N-type*

First calculation of a thermally produced characteristic of this kind was given by Mattheck[4]. He supposed a very simple and idealized model involving a material whose electrical conductivity had following behaviour

$$\sigma(T) = \sigma_1 \text{ if } T < T_c$$

$$\sigma(T) = \sigma_2 \text{ if } T > T_c, \text{ where } \sigma_1 > \sigma_2 \tag{1}$$

or, $\sigma$ had two different but constant values below and above the critical temperature $T_c$. A strip of this material of length $d$, width $h$ and of thickness $2r$ was thought to be placed between two insulating plates of the same width and length, forming thus a rectangular sandwich $2L$ thick. Heat was allowed to flow in only one direction perpendicular to the insulators while the electric field was directed along $d$-axis and was therefore perpendicular to the heat flow. Solving the heat transport equation under certain boundary conditions Mattheck obtained I—V characteristic of the device in the parametric form

$$V = \left[\frac{2\,Kd^2\,(T_c - T_0)}{\sigma_1\,(a^2 - r^2 - 2\,L\,a + 2\,L\,r + 2\,qaL - 2\,q\,a^2)}\right]^{\frac{1}{2}},$$

$$I = \frac{[2K\,(T_c - T_0]^{\frac{1}{2}}\,\{\sigma_1[2(r - a)\,h + 2\,q\,a\,h]\}}{[\sigma_1\,(a^2 - r^2 - 2\,L\,a + 2\,L\,r + 2\,qaL - 2\,q\,a^2)]^{\frac{1}{2}}}. \tag{2}$$

Here $a$ is a parameter, $T_0$ the ambient temperature, $q$ the ratio of conductivities $\sigma_2/\sigma_1$ and $K$ the thermal conductivity, presumably of equal magnitude for both the active material and the insulator. In fact, Equs. (2) represent the characteristic only between two critical voltages $V_{c1}$ and $V_{c2}$ (and critical currents $I_{c1}$ and $I_{c2}$). Namely, for $0 < V < V_{c1}$ the characteristic is a straight line since the Joule heating of the material does not affect its presumably constant conductivity $\sigma_1$. At the first critical voltage $V_{c1}$, when the hottest core of the sample reaches the temperature $T_c$, a filament of low-conductive phase will form. Its diameter $2a$ (the parameter in the equations) increases with voltage and at another critical voltage $V_{c2}$ it will be equal to $2r$, i. e. all of the material will be converted into the low--conductive phase. For $V > V_{c2}$ the I—V characteristic will again be a straight line because $\sigma_2$ does not depend upon temperature either (see the general shape of the curve shown in Fig. 4.). The range between the points ($V_{c1}$, $I_{c1}$) and ($V_{c2}$, $I_{c2}$) is the range of negative differential resistance. As the Equs. (2) show, its width is dictated solely by the conductivity ratio $q$. If it approaches zero this region extends over a large scale of currents and voltages. Contrary, for $q = 1$ there is not such region whatsoever.

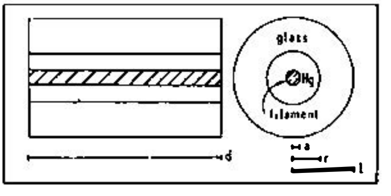

Fig. 3. Sample geometry.

## 3. *Experiment with mercury*

To examine the behaviour of a metal as an active material in which N-type characteristic can be thermally produced, an experiment with mercury was designed. This metal has $q < 1$ and offers certain manipulation convenience. A glass capilary tube (Fig. 3.) with $L = 3.50 \cdot 10^{-3}$ m, $r = 1.96 \cdot 10^{-4}$ m and $d = 0.29$m was used as a mercury container. The tube was U-formed and had a small pool at each end in which contact wires of amalgamated copper were immersed. To assure a constant ambient temperature the capilary was placed in liquid nitrogen so that $T_0$ was 77.3K. Measurements were performed with standard laboratory equipment and gave the results shown as dots in Fig. 4. As one can see the charac-

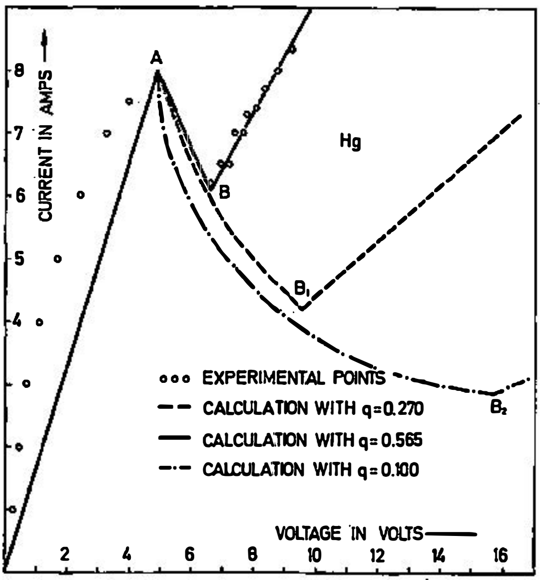


Fig. 4. I—V characteristics of a mercury sample.

teristic is established to be of N-type, but its actual shape requested additional comments. First, the characteristic is not quite complete since there are no experimental points between A and B in Fig. 4. This interval would be accessible in the experiment only under constant-voltage conditions or at least with a load line steeper than characteristic between A and B. Unfortunately the negative resistance of our sample (1 $\Omega$ or less) was comparable with or slightly lower than the resistance of the measuring circuit, so that we actually observed a fast switching from A to B. We have not insisted upon obtaining the exact shape of I—V curve. Much more interesting were the coordinates of A and B since they offer an insight into switching effectiveness.

These coordinates may be calculated by Equs. (2) adjusted to the sample geometry used in our measurements and corrected by introducing an empirical thermal conductivity $\overline{K}$. We obtained

$$V_{c1} = \left[\frac{2\,\overline{K}\,d^2(T_c - T_0)}{\sigma_1\, r\,(2L - r)}\right]^{\frac{1}{2}}, \qquad V_{c2} = \left[\frac{\overline{K}d^2\,(T_c - T_0)}{\sigma_1\, q\, r\,(L - r)}\right],$$

$$I_{c1} = \left[\frac{2\,\overline{K}\sigma_1\,\pi^2\, r^3\,(T_c - T_0)}{2L - r}\right]^{\frac{1}{2}}, \qquad I_{c2} = \left[\frac{\overline{K}\sigma_1\pi^2\, q r^3\,(T_c - T_0)}{L - r}\right]^{\frac{1}{2}}. \tag{3}$$

Quantities which can be inserted in these formulas without discussion are $T_c = 234.3\text{K}$ — the melting point of mercury, $\sigma_1 = 3.92 \cdot 10^6\ \Omega^{-1}\text{m}^{-1}$ — electrical conductivity of solid Hg at $T_c$, and $q = 0.270$[5] the ratio of conductivities of solid and liquid Hg at $T_c$. Thermal conductivity $K$ is unknown however, but it was easy to determine it as $K = 4.75\text{Wm}^{-1}\text{K}^{-1}$ requesting the equivalence of $V_{c1}$, $I_{c1}$ calculated by (3), with the coordinates of A in Fig. 4. The calculations gave $V_{c1} = 4.8\text{V}$, $I_{c1} = 8.0\text{A}$ and $V_{c2} = 9.6\text{V}$, $I_{c2} = 4.2\text{A}$ defining by the last two figures the position of the point $B_1$ in Fig. 4. Evidently, experimental point B and the calculated point $B_1$ are quite different. At the first glance this seems to be a severe disagreement making either the Equs. (3) or the measurements invalid. But the cause of the difference is in fact very simple and lies in the inadequate value of conductivity ratio $q$. The value $q = 0.270$ makes switching in Hg seem better than it really is. When, on the other hand we employed the value $q = 0.565$, an excellent agreement was found. There is nothing peculiar in the difference between the nominal and the found $q$s. Mercury is a very anisotropic solid and can have different values for $q$, including 1. The number quoted in various tables is in fact a mean value measured in the conditions when Hg solidified into the polycrystalline state. The reproducible figure, $q = 0.565$, found in our measurements may simply be a result of the preferential crystallization of Hg in the narrow capilary tube.

It remains to be explained why the experimental points in the range between $V = 0$ and $V = V_{c1}$ do not lie on the straight line but determine a curve instead. It cannot happen otherwise since the conductivity of solid mercury depends upon temperature, being its falling function, while the Mattheck's supposition was $\sigma_1 = \text{const}$.

## 4. *Prospects for the improvement of the switching by alloying*

The described experiment shows that a N-type characteristic can be easily obtained by using mercury as an active material. Its characteristic appears to be reproducible and the switching may apparently be repeated at will any number of times. But the range of currents and voltages involved in the negative differential resistance part is relatively small. The reason for this rather unspectacular property lies in the basic parameter $q$ of Hg which — as we saw — has a relatively great magnitude. If $q$ were, for instance 0.1 (point $B_2$ in Fig. 4.) the characteristic would be much improved and probably suitable for applications. Unfortunately, such results cannot be expected with any other pure metal since all of them nominally have even greater $q$ than Hg[5]. It is therefore natural to try to see whether the smaller $q$s can be achieved by alloying. Addition of a second component to the pure metal always changes its conductivity both in solid and liquid state. Since the changes in solids and corresponding liquids are not equivalent $q$ should also be dependent on alloying. Such behaviour is frequently observed, but there is no general answer to the question of what is the form of this dependence, or, how $q$ varies with some basic parameters of alloy components and their concentrations. It means that there is no theoretical guide to date for designing an alloy with minimal $q$ at a definite temperature $T_c$. One can rely only on the long-existing empirical rules. Let us mention some of them:

— the resistivity $\varrho_s$ of a binary alloy AB in which the components are mutually soluble, so as to form a single homogeneous solid phase, changes with the fractional atomic concentration $X_A$ according to the Nordheim[6] equation

$$\varrho_s = \varrho_T + S\,(1 - X_A)\,X_A, \tag{4}$$

in which $\varrho_T$ is the part of resistivity due to thermal scattering and $S$ is a constant. In order to achieve a decreasing function $q = q(X_A)$ an alloy must be chosen whose liquidis resistivity $\varrho_L$ increases with $X_A$ faster (convexly) than in Equ. (4). In this respect the alloys of the Na-Cs[7] and Hg-K[8] type could be promising. Contrary, the Pb-Sn[9] type would be quite unsuitable because, for instance, the resistivity of liquid Pb decreases with the addition of Sn. Probably the best way would be to choose the components and compositions which give the ordered alloys (intermetalic compounds). The resistivity of these, as it is well known, is considerably lower than that of disordered alloys of the same compositions. A classical example is the Cu-Au system[10] which at compositions CuAu and $Cu_3Au$ has the resistivity $\varrho_S$ only slightly greater than those of each component. Thus the alloying does not affect $\varrho_S$ while $\varrho_L$ may be changed considerably by it. However, these good systems may have a severe drawback. Namely, the irreproducibilities in the I—V characteristics could be introduced due to annealing effects;

— the resistivity $\varrho_S$ of an alloy which forms in the solid state a two-phase mixture may be expressed[11] as

$$\varrho_S = \varrho_1^{C_1} \cdot \varrho_2^{C_2(1 - bC_1)}, \tag{5}$$

where $\varrho_1$ and $\varrho_2$ are the resistivities of respective phases, $C_1$ and $C_2$ are their volume concentrations ($C_1 + C_2 = 1$), and $b$ is a small number determined empirically for each system. This equation gives a roughly linear dependence of $\varrho_S$ upon $C_s$. It is directly applicable to simple eutectic alloys, but it may be employed in more complex systems. If an alloy has one or more intermediary phases Equ. (5) applies two or more times, for each part of a given equilibrium diagram. One can see that with a proper choice of alloy components $\varrho_S$ can be made small, to give small $q$ if $\varrho_L$ is high enough. As in the previous case $\varrho_L$ should be a »convex« function of the concentration. Especially good results would be obtained with the systems whose $\varrho_L(C)$ curves have high resistivity peaks at certain compositions (liquid $Mg_3Bi_2$, for example). Various annealing effects should again be taken into account.

These two cases evidenthly show that discusion of $q$ is still possible only on the level of mere speculation since no systematic research of the resistivity of alloys at their melting points was done. The experimental data are not very abundant so that, for instance, almost nothing can be said about the behaviour of multicomponent alloys unless they are somehow included in the second case. Furthermore, the annealing effects potentially present in all the examples discussed, seem to be of special importance. The answer on the question of switching effectiveness in alloys cannot be given until the influence of these effects on $q$ in static or dynamic conditions is known. Restricting ourselves only to equilibrium values we can ascertain that small $q$s are probable. An illustrative example is the alloy Ag—28%Sn with $q = 0.13$, approaching thus the best case in Fig. 4.

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# EFEKT PREKAPČANJA U METALIMA

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Sadržaj

Jednostavni eksperiment sa živom pokazao je da se fazni prijelaz iz čvrstog u tekuće stanje metala može iskoristiti za termičko formiranje strujno naponske karakteristike N tipa, kao i za postizanje efekta prekapčanja iz stanja manjeg u stanje većeg otpora. Kao mjera za efektivnost prekapčanja javlja se parametar $q$ definiran kao omjer vodljivosti metala u tekućem i čvrstom stanju.

Što manju vrijednost ima $q$, to je prekapčanje efektivnije. U čistim metalima je vrijednost tog parametra relativno velika, ali se manje vrijednosti mogu očekivati u nekim slitinama. Provedena je diskusija empirijskih pravila za dobivanje takvih slitina.