

TRANSPORT PROPERTIES OF METALLIC GLASSES

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1. Introduction

In the last few years metallic glasses became a subject of considerable interest. These materials are amorphous alloys where amorphous is synonymous with noncrystalline. Namely these solids are like liquid metals characterized by the absence of long range order.

However the amount of the short range order in these substances is considerably higher than in liquid metals. This is due to the fact that all these alloys are metastable and therefore prepared by various rapid quenching techniques<sup>1)</sup> whereby the speeds of quenching are never high enough to prevent some short range ordering. Therefore the material is usually considered to be amorphous if there is no ordering on the scale larger than about  $10\text{\AA}$ . Apparently there is no way of knowing the exact positions of the atoms in metallic glass. The structure of the metallic glass can be given only approximately by the radial distribution function,  $RDF(r)$ , which gives the average number of atoms from some fixed point. In contrast to those of liquid metals  $RDF(r)$  of metallic glasses<sup>2)</sup> have sharper and bigger first maximum (situated at the position of nearest neighbour atoms) and split second maximum (indicating higher degree of ordering).

The properties of metallic glasses differ considerably from those of crystalline alloys. This is probably the most evident in the case of magnetic properties where the new types of magnetic ordering<sup>3)</sup> specific to the amorphous alloys have been found. On the other hand some of the properties of metallic glasses exceed those of their crystalline counterparts which makes them promising for the industrial application.

Also the transport properties of metallic glasses are rather unusual. In most of these alloys the resistivity goes through minimum and in some cases negative resistivity coefficients are found at all temperatures. In this paper we shall begin with a short discussion regarding the applicability of the theory of liquid metals on the transport properties of metallic glasses.

Furthermore we briefly list some findings about the electrical resistivity, galvanomagnetic effects, thermopower and superconductivity of these materials.

## 2. Theoretical models

The theoretical treatment of the transport properties of metallic glasses is apparently very difficult. Consequently there is no complete theory for the transport processes in metallic glasses. The similarity in the structure of metallic glass with that of the liquid metal (as seen from RDF(r)) together with the fact that both the absolute resistivity values and temperature coefficients of the resistivity ( $\alpha$ ) are approximately equal in both cases seem to indicate the applicability of the transport theory for liquid metals to the amorphous alloys.

Using the experimental fact that the mean free path (L) in most liquid metals is much greater than the interatomic distance (a) Ziman<sup>4)</sup> concluded that the actual scattering by each atom must be small even through the perturbation of the wave function is large. The same seem to be true in the metallic glasses where the conductivities are also low but still a factor of ten or more bigger than the minimum metallic conductivity. (The minimum metallic conductivity is obtained when  $\frac{L}{a} \approx 1$ .) Indeed Ziman's theory can explain the appearance of both positive and negative  $\alpha$  values in the metallic glasses. The negative  $\alpha$  value is expected when the structure factor  $I(k)$  has a maximum for  $2k_F$  (where  $2k_F$  is the Fermi sphere diameter). The decrease in the resistivity with increasing temperature is then due to thermal smearing of the structure factor. Indeed in NiP amorphous alloys the simultaneous increase in resistivity and decrease in  $\alpha$  with increasing P content (Fig.1) were interpreted<sup>5)</sup> on the basis of Ziman's model. A similar behaviour is usually observed in transition metal - metalloid alloys.

Furthermore the behaviour of  $I(k)$  is related to Debye - Waller factor. Thus  $I(k)$  will determine also the temperature dependence of the resistivity. As the Debye-Waller factor is linear in T at higher temperatures and saturates as  $T^2$  at low temperature the same temperature dependences are expected for the resistivity. Indeed similar resistivity variation is observed in several metallic glasses<sup>6)</sup>. The same model predicts the thermoelectric power linear in temperature<sup>7)</sup> and rather small. Again, similar thermopower variation is observed in some metallic glasses<sup>8)</sup>.

However there are also some difficulties in explaining the transport properties of some metallic glasses in terms of Ziman's theory. For instance this theory would predict the resistivity of liquid Fe to be about factor of two bigger than that of a liquid Ni while the resistivities of amorphous  $Fe_{80}P_{14}B_6$  and  $Ni_{80}P_{14}B_6$  are nearly the same. Furthermore, in most of the transition metal-metalloid alloys an anomalous -  $\ln T$  resistivity variation

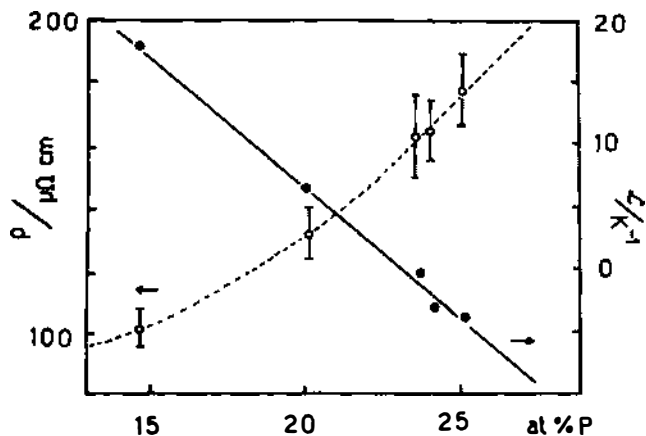


Fig.1. The resistivity ( $\rho$ ) and temperature coefficient of resistivity ( $\alpha$ ) of NiP alloys<sup>5)</sup> vs P content

is observed at the lower temperatures which cannot be easily explained by means of the theory for liquid metals. Finally we note that both positive and negative  $\alpha$  values can also be obtained on the basis of Mott's s-d scattering<sup>9)</sup>.

### 3. Resistivities of Metallic Glasses

Three types of the resistivity variation<sup>10)</sup> usually observed in the metallic glasses are schematically shown in Fig.2. In a class A the resistivity continuously increases with temperature. At low temperatures resistivity follows a  $T^2$  law while at higher temperatures it becomes linear. Such a resistivity behaviour is usually observed in metallic glasses without magnetic elements which are usually diamagnetic.

In a class B there is a resistivity minimum below which the resistivity varies as  $-\ln T$ . Thus the total resistivity can be represented as a sum of a  $-\ln T$  term and a positive contribution in a form of the power law  $(BT^n)$  with both coefficient (B) and exponent (n) depending on the temperature range. These alloys are usually paramagnetic or ferromagnetic and always contain some transition or rare earth element.

In a class C, the resistivity continuously decreases with temperature and sometimes the  $-\ln T$  variation is observed at low temperature. When this is the case the only difference between class B) and C) is in the coefficient B which is either positive or negative.

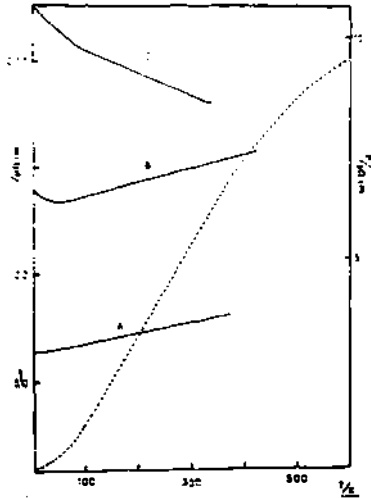


Fig.2. The resistivity variations observed in metallic glasses, and the resistivity of a pure crystalline metal (dotted line)

Limited space prevents us of discussing the resistivity variation in either of those classes in any detail. (The resistivities of class B systems are discussed in other papers<sup>11,12,13</sup> at this conference). We note that the resistivities of all these system are in general agreement with the Ziman's theory. This is probably the most evident in the case of NiP alloys where by changing the P content the resistivity behaviour changes from that of a class B) to one which is characteristic for class C systems<sup>5</sup>). (On the other hand both the resistivity minima and negative  $\alpha$  values were also found in some disordered crystalline alloys<sup>14</sup>) with a rather high transition metal content).

However, the resistivity minimum and  $-\ln T$  resistivity variation below the minimum cannot be simply explained by Ziman's theory. Several theoretical models have been proposed in order to explain the  $-\ln T$  resistivity variation. We note that  $-\ln T$  resistivity dependence is observed only in metallic glasses with transition metal as the component. Therefore it was thought that these

anomalies are caused by the magnetic effects<sup>15,16,17,18</sup>). However as in most of metallic glasses the magnetic field does not change the temperature dependence of the resistivity the structural model<sup>19,20</sup>) was applied to the resistance anomalies in amorphous alloys<sup>21,22</sup>). At moment it is difficult to say which of these models is most likely to be true. In fact in some alloys<sup>23</sup>) "magnetic" models seem to be more appropriate while in some others<sup>24</sup>) the structural ones may be adequate.

Another interesting point is the limiting resistivity variation at the lowest temperatures. Recent investigations<sup>25,26</sup>) have shown that the resistivity of metallic glasses tends to saturate as  $\sim T^2$  when  $T \rightarrow 0$ . These results<sup>26</sup>) put a stringent criterion on any future calculation of resistivity for these alloys. Theory which does not predict the saturation of the resistivity at the lowest temperatures cannot be regarded as satisfactory.

There are only few accurate measurements of the resistivities of metallic glasses at high temperature and therefore we will not discuss them here in any detail (Additional information can be obtained from Refs. 8, 12 and 13). We note however that although the resistivity of metallic glass at higher temperatures may possibly be described<sup>8</sup>) in terms of Ziman's model, in the magnetic alloys there is also a significant magnetic contribution to the resistivity<sup>12,13</sup>).

#### 4. Galvanomagnetic effects

The investigation of the Hall effect and magnetoresistivity can help the better understanding of the electronic structure of the metallic glasses. Unfortunately the measurements of either of these properties are neither systematic nor numerous.

In Fig.3 we show<sup>27</sup>) the Hall effect measurements on two amorphous ferromagnets and one nonmagnetic metallic glass. It can be seen that in nonmagnetic alloy the Hall voltage is rather small and negative. Thus experimentally the free electron model seem to be rather succesfull in explaining the ordinary Hall constant. It also seems that the d-electrons do not contribute much to the conductivity in metallic glasses. In the amorphous ferromagnets the Hall voltage is rather large and can be separated into the normal and extraordinary part<sup>28</sup>). The extraordinary Hall effect is largely predominant in metallic glasses. This comes from the fact that the extraordinary Hall effect results from the spin-orbit coupling through asymmetries of the scattering and is

therefore an increasing function of the number of scatterers (resistivity). Thus the Hall effect can be conveniently used for the investigation of magnetic properties of metallic glasses.

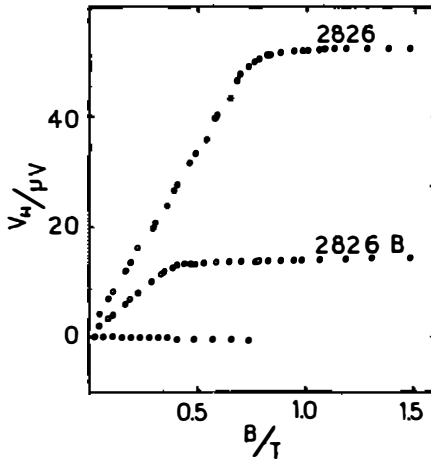


Fig.3. Hall voltages<sup>27)</sup> vs applied field: ○ Metglass alloys, ● PdCuSi alloy

There are only few measurements of the magnetoresistivity mainly in the amorphous ferromagnets. In this case the magnetoresistance should consist from the normal part (Lorentz force) and that due to spontaneous magnetization. For some amorphous ferromagnets<sup>29)</sup> the magnetoresistance is similar to that of the soft crystalline magnets (apart from the fact that the normal part seems negligible). A more detailed discussion of the magnetoresistance of some Fe-Ni based metallic glasses is given elsewhere<sup>28)</sup> at this conference.

##### 5) Superconductivity

A number of amorphous superconductors have been reported. These materials are rather important because of their potential application. Namely in some cases the amorphous superconductors can be desirable due to the fact that they may be less sensitive to the radiation. So far the amorphous superconductors appear to have in general lower critical temperatures than their crystalline

counterparts. More important for a practical superconducting material is the critical current density ( $J_c$ ) and its dependence on the magnetic field. So far in the metallic glasses the  $J_c$  values appear to be lower and decrease more rapidly with magnetic field than in the best crystalline superconductors. The small values of  $J_c$  are probably related to the disordered structure. Namely because the disorder is on a scale smaller than the coherence length there are no favourable centers for the flux pinning. That this may be the case seems confirmed by the fact that when partially crystallized these alloys show improved characteristics.

#### 6. Thermoelectric power and thermal conductivity

The thermopower<sup>8)</sup> measurements should in principle enable us to single out the theoretical model which is most successful in explaining the transport properties of metallic glasses. Unfortunately there are only few measurements of the thermoelectric power of the metallic glasses in a more extended temperature range.

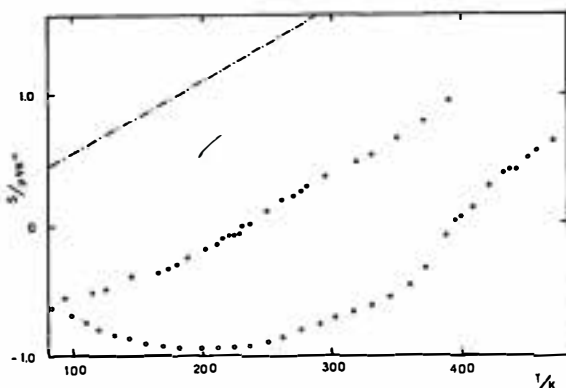


Fig.4. Thermoelectric power vs temperature: • Fe<sub>20</sub>Ni<sub>60</sub>P<sub>14</sub>B<sub>6</sub>, ○ Fe<sub>30</sub>Ni<sub>50</sub>P<sub>14</sub>B<sub>6</sub>. Dotted line<sup>8)</sup> shows the thermopower of Be<sub>40</sub>Ti<sub>50</sub>Zr<sub>10</sub> alloy

In Fig.4 we show the thermoelectric powers of two Fe<sub>x</sub>Ni<sub>80-x</sub>P<sub>14</sub>B<sub>6</sub> alloys (with  $x = 20$  and  $30$ ) and a part of the thermoelectric power of Be<sub>40</sub>Ti<sub>50</sub>Zr<sub>10</sub>. While the thermoelectric power of the nonmagnetic Be<sub>40</sub>Ti<sub>50</sub>Zr<sub>10</sub> alloy seem to be well described by Ziman's model (chapter 2), the thermopower variation in Fe<sub>x</sub>Ni<sub>80-x</sub>P<sub>14</sub>B<sub>6</sub> alloys is quite different<sup>13)</sup>. This difference seem to be due to different magnetic properties of these alloys and it seem to show that no single theory can successfully explain the transport properties of all metallic glasses.

For the sake of completeness we also note that there have been made few measurements of the thermal conductivity which are listed in Ref.30.

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