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To cite this version:
M. Očko, E. Babić. Transport properties of Ni81.5B18.5 - YP y amorphous alloys. Journal de Physique, 1989, 50 (21), pp.3233-3242. <10.1051/jphys:0198900500210323300>. <jpa-00211139>

HAL Id: jpa-00211139
https://hal.archives-ouvertes.fr/jpa-00211139
Submitted on 1 Jan 1989

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Transport properties of Ni$_{81.5}$B$_{18.5}$ - $y$Py amorphous alloys

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Résumé. — Nous avons étudié le pouvoir thermoélectrique (PTE) d’alliages amorphes non magnétiques Ni$_{81.5}$B$_{18.5}$ - $y$Py ($y = 0, 1.8, 3.7, 7.4, 13, 16.8$ et $18.5$ at % P) entre 77 K et 350 K ainsi que la résistivité et son coefficient de température. Nous interprétons simultanément ces propriétés dans le cadre d’un modèle de Ziman généralisé. Nous choisissons, pour ces calculs, des déphasages qui reflètent le remplissage de la bande d des alliages tel qu’on le déduit des mesures de chaleur spécifique. On obtient une surprenante contribution négative importante dans les alliages riches en bore. On discute l’origine possible d’une contribution géante au PTE de ces alliages.

Abstract. — The thermoelectric power of the amorphous nonmagnetic alloy system Ni$_{81.5}$B$_{18.5}$ - $y$Py ($y = 0, 1.8, 3.7, 7.4, 13, 16.8$ and $18.5$ at % P) has been investigated in the temperature range between 77 and 350 K. The resistivity and temperature coefficient of resistivity have also been measured. The high temperature slope of the thermopower, the resistivity and the room temperature coefficient of resistivity are simultaneously explained within the framework of the extended Ziman model. In performing the corresponding calculations we have chosen the phase shifts in such a way that they reflect the d-band filling on alloying (deduced from the specific heat measurements). An unexpectedly large negative thermopower is obtained for the boron rich alloys. A possible origin of a « giant » contribution to the thermopower of these alloys is discussed.

1. Introduction.

Several theoretical approaches have been used in order to explain the transport properties of transition metal based alloys. These range from the Ziman and the Mott model, via the concept of d-electron contribution to conductivity to recently introduced quantum coherence effects. In spite of this effort the problem has not been completely solved yet.

Here we focus our attention to the difficulty in obtaining mutually consistent results for the residual resistivity ($\rho$), the temperature coefficient of resistivity (TCR) and the thermoelectric power (S) within the framework of the extended Ziman model [1]. Some objections to the earlier calculations based on the Ziman model are listed below.

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Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:0198900500210323300
In the earlier calculations there was an inconsistency in the determination of the number of conducting electrons \( (Z_c) \). For example \[2\] the electronic configuration \( 3d^94s^1 \) has been selected in calculating the phase shifts, whereas 0.5 electron per Ni atom was taken to fill the conduction band. A good result for the residual resistivity and the correct sign of the thermopower were obtained in the case of NiP amorphous alloys. However, the concentration dependence of the thermopower was not correct. Such an inconsistency was removed by applying Lloyd’s formula \[3\] and some relatively good results for residual resistivity were obtained, but that generated too large a number of conducting electrons \( (Z_c > 2) \) \[3, 4\]. Indeed, the Hall effect measurements rarely yield \( Z_c > 1 \) for the nonmagnetic transition metal (TM) based alloys \[5\]. Similary, from the magnetization results \[6\] on magnetic TM alloys one can also conclude that the number of conduction electrons has to be small (because some of them have to fill the d-band, leaving a relatively small number of holes). Accordingly, the magnetization as well as the specific heat measurements \[7\] clearly show that the electronic configuration of the transition metal atoms in TM alloy is changed on alloying, therefore the calculation of the phase shifts based on the assumed \( 3d^94s^1 \) electronic configuration is not justified. Indeed, the available results \[7, 8\] might lead to a conclusion that an electron being scattered on transition metal atom does not see the simple \( 3d^94s^1 \) electronic configuration.

The applicability of the Boltzmann equation to the amorphous alloys with a very short electronic mean free path should also be carefully considered. However, some experimental evidence \[9\] indicates that the Ziman theory provides a reasonable description even for the high resistivity alloys.

Furthermore, depending on the density of d-electron states at the Fermi level one may also consider the d-electron contribution to conductivity (not included in the Ziman or Mott model).

Bearing in mind the above remarks we singled out the non-magnetic amorphous alloy system \( \text{Ni}_{81.5}\text{B}_{18.5-y}\text{P}_{y} \) as a suitable candidate in order to perform the calculation of transport properties, taking into account the effect of d-band filling. Several measurements \[7, 8, 10\] performed on NiPB alloy system can be explained by the use of the rigid band model, thus the shape of the 3d-band may, in principle, be reconstructed.

Although we have performed earlier the resistivity measurements, we are aware that the eventually successful explanation of the resistivity alone may not be sufficient to decide whether the proposed approach is correct or not. Therefore we have also performed the detailed measurements of the thermoelectric power.

2. Experimental results.

The samples have been prepared and checked for amorphousness at the Central Research Institute for Physics, Budapest, Hungary. The experimental details concerning the resistivity measurements are given elsewhere \[11\]. The uncertainty in the absolute value of the resistivity has been a few percent. In order to minimize the error we have deduced the cross-section of the samples from the mass, length and density measurements. Above 100 K the resistivity increases linearly with temperature thus allowing the unambiguous determination of the temperature coefficient of resistivity (TCR). The uncertainty in TCR has been a few percent as well as deduced from the measurements on several samples of the same alloy.

The thermopower has been measured relative to pure lead from the liquid nitrogen temperature up to 350 K. The differential method has been used. The volage connections have been made by copper wires having the diameter of 30 \( \mu \text{m} \) fixed on the sample by silver-paint. The difference in temperatures of the posts has been measured by chromel-constantan thermo-couples. The absolute thermopower of the sample has been obtained by substracting
the absolute thermopower of the lead standard [12] from the measured relative thermopower. The accuracy of the final thermopower result has been within 0.1 μVK⁻¹.

The results are shown in figure 1. They are in agreement with the available results [10, 13]. The main features of the thermopower behaviour are as follows:

i) the thermopower is positive for \( y \geq 13 \) at % P;

ii) it is linear within the whole temperature range for \( y \geq 7.4 \) at % P;

iii) it is nonlinear (similar to that of ferromagnet in the low temperature region) for \( y \leq 3.7 \) at % P;

iv) for \( y = 1.8 \) at % P the thermopower reaches unexpectedly large negative values, even larger than those found in amorphous ferromagnets [14, 15].

Fig. 1. — Thermopower of amorphous Ni₈₁.₅B₁₈.₅₋₉P₉ alloys vs. temperature. The thermopower of Ni₈₁.₅B₁₇P₁₆.₈ is omitted for clarity.

The magnitude and temperature dependence of the thermopower for \( y \geq 7.4 \) at % P is consistent with the expected behaviour from the Ziman theory and is confirmed by our calculations (Fig. 1, Tab. I). The problems arise for the concentrations \( y \leq 3.7 \) at % P. The experimental results indicate the existence of two contributions to the thermoelectric power. One of these contributions causes a strong increase of the thermopower up to 90 K. This contribution is much more pronounced in the alloys with \( y \leq 3.7 \) at % P but seems to exists in all NiPB alloys. Above 100 K the thermopower becomes more or less linear, indicating that the first (low temperature) contribution to the thermopower remains roughly constant at higher temperatures. Therefore the average gradient of thermopower above 100 K \(((\Delta S/\Delta T)^{H:T}\) in Tab. I) reflects the second contribution to the thermopower which we ascribe.
Table 1. — Experimental and calculated results for the transport coefficients of the amorphous Ni$_{81.5}$B$_{18.5-y}$P$_{y}$ alloys: rate of change of the high temperature thermopower, $(\Delta S/\Delta T)^{H.T.}$; estimate of the rate of change of the low temperature thermopower, $(\Delta S/\Delta T)^{L.T.}$; rate of change of the thermopower calculated from the Ziman theory, $(S/T)$ — corresponds to $(\Delta S/\Delta T)^{H.T.}$; $\rho$ and $\alpha$ are the residual resistivity and the temperature coefficient of resistivity respectively.

<table>
<thead>
<tr>
<th>y at% P</th>
<th>$(\Delta S/\Delta T)^{H.T.}$ nVK$^{-2}$</th>
<th>$(\Delta S/\Delta T)^{L.T.}$ nVK$^{-2}$</th>
<th>$\rho$ $\mu\Omega$ cm</th>
<th>$\alpha$ $10^{-4}$ K$^{-1}$</th>
<th>$(S/T)$ nVK$^{-2}$ $\mu\Omega$ cm</th>
<th>$\alpha$ $10^{-4}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-16</td>
<td>-56</td>
<td>70</td>
<td>2.4</td>
<td>-13.2</td>
<td>82.3</td>
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<td>-33</td>
<td>84</td>
<td>2.0</td>
<td>-10.3</td>
<td>85.3</td>
</tr>
<tr>
<td>3.7</td>
<td>-7</td>
<td>-18</td>
<td>92</td>
<td>1.9</td>
<td>-9.0</td>
<td>89.0</td>
</tr>
<tr>
<td>7.4</td>
<td>-3</td>
<td>-8</td>
<td>101</td>
<td>1.5</td>
<td>-5.9</td>
<td>95.9</td>
</tr>
<tr>
<td>13.0</td>
<td>+3</td>
<td>+2</td>
<td>106</td>
<td>1.1</td>
<td>-1.3</td>
<td>108.8</td>
</tr>
<tr>
<td>16.8</td>
<td>+6</td>
<td>+6</td>
<td></td>
<td></td>
<td>+1.9</td>
<td>121.7</td>
</tr>
<tr>
<td>18.5</td>
<td>+8</td>
<td>+10</td>
<td>112</td>
<td>0.8</td>
<td>+3.1</td>
<td>124.3</td>
</tr>
</tbody>
</table>

to be the Ziman contribution. Such an extraction of the (high temperature) term proportional to temperature can be found in the literature [16-18], too. We note that a pure Ziman term would be expected for $T > \theta_D$ (i.e. $T > 300$ K for our alloys). However, a linear variation of the thermopower above 100 K seems to justify the interpretation of $(\Delta S/\Delta T)^{H.T.}$ as the Ziman term.

Firstly we shall focus our attention on the first (low temperature) contributions to the thermopower. Unfortunately, at this stage, we can only list some possible explanations of the low temperature contribution to the thermopower (represented by $(\Delta S/\Delta T)^{L.T.}$ in Tab. I).

As the resistivity decreases the electronic mean free path increases and so, the dividing of the electrons to s and d-like has more sense. In these circumstances the Mott theory can be applicable and may lead to large thermopower values (Tab. I). Some investigations [7, 8] indicate that the electronic band structure of our alloy system is Pd-like, and Pd has a large negative thermopower well explained by the Mott theory.

Moreover, there is a suggestion [10] that the thermopower of amorphous NiBP alloys can be explained by the Mott theory over the whole concentration range. Namely, both the experimental results and the calculations of the density of state (DOS) [19] imply that the d-band is open through the whole concentration range. However, in order to explain a positive thermopower by the Mott theory, there has to exist a minimum in the electronic DOS at the Fermi level ($E_F$). For our alloys, the DOS at $E_F$ smoothly varies on alloying [7] which, means, in terms of the rigid band model (used in the explanation of some properties [7, 8]) a smooth variation of the density of states with energy. Hence, it is hard to believe that a minimum in the DOS at $E_F$ exists in the amorphous NiBP alloys. The theoretical calculations [19] confirm such a conclusion.

No phonon drag contribution to the thermoelectric power is expected in amorphous solid [20]. However, one can argue that the phonon drag term may become observable if there were empty states for an electron to be scattered. This may yield that the phonon-electron
scattering contributes to the thermopower even in the amorphous alloys. Accordingly, the phonon drag term could be larger in the alloys with an open 3d-band. Since in NiBP alloys 3d-states are more open on the boron rich side the phonon drag could, perhaps, contribute to the thermopower of these alloys. The increase of \((\Delta S/\Delta T)^{L.T.}\) towards boron-rich side of NiBP alloy system is the main reason why we have put forward the phonon drag contribution to the thermopower as a possibility.

As the more probable source of large \((\Delta S/\Delta T)^{L.T.}\) in boron-rich alloys we mention the possible ferromagnetic clusters which might behave like a giant moments giving a large thermopower. (Note that on the boron-rich side we reach the region of the critical concentration for the formation of the amorphous state [7, 21]). Furthermore, the magnetic measurements [8] indicate the presence of strong intrinsic spin-fluctuations at low temperatures in the boron-rich alloys. Thus the proximity of ferromagnetism could be the origin of a large \((\Delta S/\Delta T)^{L.T.}\) in these alloys. The complex temperature dependence of the thermopower for low phosphorous concentrations is also most likely due to magnetic scattering.

As the last possible explanation of a large thermopower we mention the electron-phonon mass enhancement. However, it is hard to believe that it gives such a large negative contribution. This effect might, however, be the reason why the high temperature thermopower of the alloys with \(y \geqslant 13\) at \(\%\) P does not extrapolate to zero value [20].

At this stage, we cannot tell conclusively what is the origin of a large termopower in some of our alloys. (We are looking for an experiment which would elucidate the origin of the low temperature thermopower). Nevertheless, all of the above mentioned mechanisms are not of great importance at higher temperatures. Hence, the rate of change of the thermopower \((\Delta S/\Delta T)^{H.T.}\) (Tab. I) with temperature at higher temperatures reflects mainly the diffusion thermopower which we shall try to explain within the framework of the Faber-Ziman theory.

### 3. Calculations.

Within the framework of the extended Ziman theory the residual resistivity can be expressed in the form [22]:

\[
\rho = \frac{30 \pi^3 \hbar^3 / me^2}{\Omega_0 k_F^2 E_F} c_{Ni} \left( \sin^2 \delta_2 + \frac{1}{5} \sin^2 \delta_0 \right) S_T(2k_F).
\]  

(1)

The thermopower is given by [22]:

\[
S = \frac{\pi^2 k_B^2 T}{3 |e| E_F} (-2 + w + z)
\]

(2)

with

\[
w = \frac{k_F}{S_T(2k_F)} \left( \frac{\partial S_T}{\partial k} \right)_{2k_F}
\]

(2a)

and

\[
z = \frac{k_F \sin 2 \delta_0 \frac{\partial \delta_0}{\partial k} + 5 \sin 2 \delta_2 \frac{\partial \delta_2}{\partial k}}{2 \sin^2 \delta_0 + 5 \sin^2 \delta_2}.
\]

(2b)

Where \(\Omega_0\) is the volume per atom, \(k_F\) is the Fermi wave number, \(E_F\) is the Fermi energy, \(m\) is the electronic mass. \(c_{Ni}\) is the concentration of Ni. As is usual in the case of the alloys with a
high concentration of the transition metal, we ignore here the direct influence of metalloids, but as the Fermi level approaches the end of the 3d-band it is expected that besides the $\delta_2$ phase shift contribution, the contributions from $\delta_0$ and $\delta_1$ become important as well. For the sake of simplicity we choose $\delta_1 = 0$ which will be discussed later. Also, we suppose that the backward scattering is of the main importance.

The temperature coefficient of resistivity $\left( \alpha = \frac{1}{\rho} \frac{\partial \rho}{\partial T} \right)$ is given by [23]:

$$\alpha = 2 \left( 1 - \frac{S_T(2k_F)}{S_T(2k_F)} \right) \frac{\partial W(T)}{\partial T} = 8 \left( 1 - \frac{S_T(2k_F)}{S_T(2k_F)} \right) \frac{3 \hbar^2 k_F^2}{2 M k_B \theta_D}$$

where $W(T)$ is the Debye-Waller factor, $M$ is atomic mass and $\theta_D$ is the Debye temperature.

Hereafter follow the explanations of how we determine the physical quantities in the above expressions. We have calculated the structure factor for each alloy from the Percus-Yevick model of dense random packing of hard spheres using the Goldsmidt radii. A justification for the use of Percus-Yevick model (taken from liquid alloys) lies in the fact that the first peak of the structure factor $S_T(Q)$ (inside of which there is the $2k_F$) is practically of the same shape in both liquid and amorphous alloys. Total packing fractions $\eta$, mean atomic volumes (calculated in the usual manner [24]) and the structure factors, taken at $2k_F$, are given in table II. The values of $\eta$ are very close to the values obtained by other authors for the similar amorphous alloy systems [4]. Theoretical structure factor for Ni$_{81.5}$P$_{18.5}$ fits well the experimental one around the first maximum [25]. In order to calculate the other parameters we have to calculate the number of conducting electrons. We take that B gives one and P three electrons. These electrons are shared between the conduction band and the d-band of Ni atom. Here, we try to accept the experimental fact that the 3d-band is filled on substituting P for B. Moreover, supposing that the number of electrons transferring into the 3d-band is proportional to the density of states, we come to the fact that more electrons transfer to the d-band than to the conducting band. In particular, the number of d-electrons per transition metal atom is calculated from the expression: $Z_d = 9.12 + \Delta Z_0 (1 - 0.28/g(E_F)/c_{Ni})$ and the number of conducting electrons from the expression: $Z_c = 0.88 \cdot 0.815 + 0.28 \Delta Z_0/g(E_F)$, where $\Delta Z_0 = 1 \cdot (0.185 - y) + 3 y$ is the number of electrons given by the metalloids at the given concentration. $g(E_F)$ is the density of states of Ni and $g(E_F)$ is the density of states of Cu (0.28 eV$^{-1}$ at$^{-1}$) represents the density of states of s-electrons. The specific heat measurements on the Ni-based amorphous alloys [7] indicate

Table II. — Calculated quantities used as the parameters in the extended Ziman theory.

<table>
<thead>
<tr>
<th>$y$ at% P</th>
<th>$\eta$</th>
<th>$\Omega_0$ $10^{-30}$ m$^3$</th>
<th>$S(2k_F)$</th>
<th>$g(E_F)$ eV$^{-1}$ at$^{-1}$</th>
<th>$Z_0$</th>
<th>$Z_c$</th>
<th>$Z_d$</th>
<th>$k_F$ $10^{10}$ m$^{-1}$</th>
<th>$E_F$ cV</th>
<th>$\delta_0$ rad</th>
<th>$\delta_2$ rad</th>
<th>$w$</th>
<th>$z$</th>
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<tbody>
<tr>
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<td>0.1732</td>
<td>1.531</td>
<td>0.185</td>
<td>0.7436</td>
<td>9.3146</td>
<td>1.28637</td>
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<td>1.1680</td>
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<td>-5.40</td>
</tr>
<tr>
<td>1.8</td>
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<td>10.419</td>
<td>0.1840</td>
<td>1.442</td>
<td>0.221</td>
<td>0.7504</td>
<td>9.3504</td>
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<td>0.1968</td>
<td>1.399</td>
<td>0.259</td>
<td>0.7579</td>
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<td>1.1905</td>
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<td>-4.98</td>
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<td>0.2216</td>
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<td>0.333</td>
<td>0.7732</td>
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<td>-4.09</td>
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<td>10.946</td>
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<td>0.521</td>
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<td>6.4709</td>
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<td>-2.37</td>
</tr>
<tr>
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<td>11.119</td>
<td>0.3219</td>
<td>1.026</td>
<td>0.555</td>
<td>0.8276</td>
<td>9.6655</td>
<td>1.30134</td>
<td>6.4606</td>
<td>1.3000</td>
<td>3.0365</td>
<td>+4.88</td>
<td>-2.07</td>
</tr>
</tbody>
</table>
that when the d-band is full, the DOS at the $E_F$ tends to the value corresponding to crystalline Cu.

We note here that recent Hall effect results support the idea of d-band filling in amorphous Ni-based alloys. In particular, in NiBSi alloys the number of conduction electrons initially increases faster than the number of electrons given by metalloids [5]. Clearly, the number of electrons filling the 3d-band decreases with increasing metalloid content, due to the shape of the density of states.

The number of conduction electrons per Ni atom that we use is 0.88 taken from Jaswal's calculation [26]. Hence, there are 9.12 d-electrons per Ni atom. The density of states at the Fermi level for « paramagnetic Ni » is also needed. The value $2.4 \text{ eV}^{-1} \text{ at}^{-1}$ was estimated by extrapolating Kuentzler's [7] results for specific heat of our system. The Fermi wave number and the Fermi energy were calculated within the free electron model [1, 2, 4]. These values are given in the table II. We emphasize again, that the experimental results [7, 8] clearly indicate the filling of the d-band and, that a such simple way of calculating the number of s and d-electrons is due to the fact that the rigid band model seems applicable to our alloy system, although the band calculations [19, 26] indicate a hybridization effect. However, the main features of the DOS around $E_F$ do not change upon hybridization: i) $E_F$ is on the right-side of the very steep part of the DOS; ii) As P-content increases, $E_F$ is moving to the right-hand side (to the larger values), and hence, the DOS at the $E_F$ becomes lower. These are the main features of the rigid band model too. The above picture is obtained by the band calculations for NiP amorphous alloys [19, 26]. For our NiBP system (where the content of the transition metal is constant) it is very likely that this picture remains the same (moreover, the disturbance due to the hybridization ought to be smaller). This is probably the reason why the properties depending only on the characteristics of the DOS at the $E_F$ may be interpreted within the rigid band model [7]. Here we wish to stress again that the experimental results [7, 8], and the band calculations [19, 26] clearly indicate that even in the Ni$_{81.5}$P$_{18.5}$ the d-band is not full and that the $E_F$ is on the right-hand side of a steep portion of the DOS.

As has already been pointed out in the introduction, the electronic configuration of Ni atom 3d$^9$ 4s$^1$ is meaningless, due to the filling of the 3d-band. For this reason we make an estimation of the phase shifts rather than perform the usual calculations by assuming 3d$^9$ 4s$^1$ or some other electronic configuration. Our estimations are:

$$
\delta_2 = \frac{\pi}{10} Z_d; \quad \delta_0 = \frac{\pi}{2} Z_c; \quad \delta_1 = 0.
$$

The choice for $\delta_2$ is consistent with that found in the literature [27]. $\delta_1 = 0$ is an arbitrary choice, but $\delta_1$ has to be small because of the small number of p-electrons. We have constructed $\delta_0$ in the same spirit as $\delta_2$. A similar way of selecting the phase shifts $\delta_0$ and $\delta_1$ can be found in the literature [28]. There, $\delta_0$ and $\delta_1$ were closely related to the number of s and p-electrons. Here we have taken the direct proportionality between the phase shifts and the number of corresponding electrons (as in the case of $\delta_2$ phase shift).

There comes out one fact connected to such a choice of the $\delta_2$ phase shifts. As $Z_d$ is the number of the d-electrons per transition metal atom which depends on particular alloy, we may say that the effective charge transfer to the d-band is taken into account. The calculations based upon the 3d$^9$ 4s$^1$ electronic configuration cannot take into account the effect of the charge transfer.

Assuming the validity of the rigid band model it is easy to determine $\partial \delta_0/\partial k$ and $\partial \delta_2/\partial k$. From the values given in the table II we have obtained $8.82 \times 10^{-10}$ radm and $7.36 \times 10^{-10}$ radm for $\partial \delta_0/\partial k$ and $\partial \delta_2/\partial k$, respectively. From the calculated structure factors (Tab. II) we have also determined $\partial S(2k_F)/\partial k$ for all alloys.
Substituting the quantities discussed above and the Debye temperatures taken from the literature [7] into the expressions (1), (2) and (3) we have obtained the values for the residual resistivity, the thermopower and the temperature coefficient of the resistivity for the amorphous Ni$_{81.5}$B$_{18.5-y}$P$_y$ alloys. A correlation between the experimental and theoretical results can be seen in table I and in figure 2.

![Graph showing rate of change of high temperature thermopower, calculated thermopower, residual resistivity, and temperature coefficient of resistivity vs. concentration.](image)

Fig. 2. — Rate of change of the high temperature thermopower ($\Delta S/\Delta T$)$_{H.T.}$ and the calculated thermopower ($S/T$) form the extended Ziman theory, residual resistivity ($\rho$) and the temperature coefficient of resistivity ($\alpha$) of amorphous Ni$_{81.5}$B$_{18.5-y}$P$_y$ alloys vs. concentration. Solid symbols are experimental and open symbols are theoretical results.

As far as we know, there are no calculations for the amorphous alloys containing transition metal which give the correct concentration dependence even of only two of transport coefficients ($\rho$ and $S$) calculated. Hence, we think that the results giving the right concentration dependence of three transport coefficients are significant.

Of course, since the extended Ziman theory is very sensitive on the parameters used, it is clear that the whole agreement will be destroyed if one changes the values of the parameters used. However, the parameters which we have used are either natural ($Z_B = 1$ and $Z_p = 3$), or experimentally controlled ($Z_c$ by the DOS), or taken from literature (the density of the states of « paramagnetic Ni »). On the other hand, the calculations reflect a clear physical picture: moving from the boron-rich side to the phosphorous-rich side the number of electrons increases and hence $E_F$ increases as well. Thus $E_F$ is shifted from the region where the DOS dominates giving the negative thermopower to the region where the scattering described by the structure factor dominates, giving the positive thermopower. Such an interplay of $z \sim \partial g(k_F)/\partial k$ and $w \sim \partial S(2k_F)/\partial k$ can be seen in table II.
For the residual resistivity the agreement between our calculated values and the experimental values found in the literature [10] is even better comparing to our results.

There is great discrepancy in TCR values for which the concentration dependence of the experimental and theoretical results is the same, but the experimental values are systematically lower than the theoretical ones. Although the approximation involved in the derivation of the equation (3) may cause this discrepancy, it seems to us that we have overestimated, by our simplified procedure the number of electrons transferring to the d-band and hence we have obtained a little bit smaller value of $k_F$ than expected. The sensitivity of TCR on the actual $k_F$ value is clearly demonstrated in tables I and II. Furthermore, the incipient localization (not accounted for in the calculation) may also lower the measured TCR value. The Mooij [29] type of correlation between the magnitude of resistivity and TCR seems to support this view. However, the resistivity itself (which is not large in our alloys : $\rho < 150 \mu \Omega \text{cm}$) should be dominated by the classical (Ziman's) contribution [30]. Although the calculated TCR values are (on average) five times larger than the experimental ones, the concentration dependence is correct. The aim of our calculations has not been to obtain the accurate value of the particular transport coefficient for a given alloy, but to obtain the correct concentration dependence for all three transport coefficients within the same model and with the same parameters used.

4. Summary and conclusion.

We pointed out one possible reason why calculations based on the extended Ziman model usually do not yield mutually consistent results for the transport properties of the amorphous TM-based alloys.

There is clear experimental evidence indicating 3d-band filling on alloying in the alloys of the late 3d-metals with metalloids. In order to perform a quantitative estimations of the influence of this effect on the transport properties of these alloys we have chosen a nonmagnetic amorphous alloy system Ni$_{81.5}$B$_{18.5-y}$P$_y$ (0 $\leq y \leq 18.5$). Systematic measurements of the residual resistivity, temperature coefficient of resistivity and thermopower have been performed. We have also calculated the above properties within the framework of the extended Ziman model, but in these calculations we have included, in a simple manner, the effect of alloying. A good agreement between the experimental and theoretical results has been obtained. The (quantitative) agreement is particularly good in the case of the residual resistivity and in the case of the high temperature slope of the thermopower, whereas the experimental coefficients of resistivity are systematically lower than the calculated ones. The discrepancy in TCR values is probably due to a small underestimation of $k_F$ values, but some contribution of the incipient localization to the measured TCR cannot be ruled out.

In summary, the extended Ziman model appears to be capable to explain the transport properties of nonmagnetic Ni-based amorphous alloys, provided that the alloying effects are taken into account. Of course, this conclusion may not be justified in the case of the alloys with very large d-electron density of states at Fermi level. In that case the calculations which include d-electron contribution to the conductivity may be necessary. Similarly, in the case of very high resistivity ($\geq 150 \mu \Omega \text{cm}$) the incipient localization may affect the resistivity variation with temperature.

Finally, we mention the problem of very large thermoelectric power of the boron-rich NiBP and NiBSi alloys, which deserves some further investigation.

Acknowledgements.

We are grateful to Dr. I. Bakonyi for giving us the samples and sending us his results. One of
us (M. O.) wants to express a great appreciation to Dr. Láslo Forró for constant help and support during this work. We thank the referees for their helpful comments.

This work was supported by N.B.S. (project N° 689).

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[26] JASWAL S. S., Phys. Rev. B 34 (1986) 8937. In fact we have taken this value from Jaswal’s calculations for the amorphous Ni81B19 for the Ni atoms surrounded by Ni atoms only. One can take this number as an adjustable parameter. In that case still better overall agreement with experimental results would be obtained if somewhat larger value for the number of conduction electrons per Ni atom was used.