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## Thermopower of $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$ amorphous alloys

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**Abstract.** The thermopower of the  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloy system with a metalloid concentration ranging from 20 to 39 at. % has been measured from 77 up to 300 K. The thermopower, as well as the specific heat, clearly shows filling of the d band on increasing metalloid content. The thermopower is negative for  $x \geq 70$  and increases rapidly as  $x$  decreases. For  $x \leq 67$  the thermopower is positive and decreases slightly with decrease in  $x$ . The high-temperature slope of the thermopower, the residual resistivity and the room-temperature coefficient of resistivity are simultaneously explained within the framework of the extended Ziman theory. In performing the corresponding calculations we have chosen the phase shifts deduced in such a way that they reflect the d-band filling on alloying (deduced from the specific heat measurements). We have also used Hall effect measurements which determine the number of conduction electrons. For  $x \geq 78$  the Ziman contribution to the thermopower is concealed by the large extra term which can be ascribed to magnetic fluctuations.

### 1. Introduction

The discussion to what extent the extended Ziman theory is applicable to the calculations of transport properties of amorphous alloys containing transition elements is still continuing. One of the first works which has placed in doubt the application of the Faber–Ziman model for the explanation of transport properties of strong-scattering amorphous alloys (Esposito *et al* 1978) has emphasised the inconsistency in the choice of the effective valence  $Z^*$  and the other relevant parameters. However, in our opinion (Očko and Babić 1989), part of the problem lies in the method of determining the phase shifts. In the earlier papers the phase shifts were calculated under the premise of the simple atomic structure which does not take into account the filling of the d band on alloying with metalloids. For example, in the case of Ni, the electronic structure of a neutral Ni atom,  $3d^94s^1$ , used to be taken (Dreirach *et al* 1972).

Recently, the uncritical use of the nearly-free-electron (NFE) model for the calculations of electron transport in amorphous alloys containing transition metals was criticised (Howson and Gallagher 1988). The NFE model is a basic supposition of the Faber–Ziman theory. The drastic changes in the free-electron density of states is what might be expected owing to the s–d hybridisation.

However, there are some systems of amorphous alloys containing 3d elements which,

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it seems, might be explained within the framework of the Faber–Ziman theory. Recently it was shown, on the basis of the resistivity and the Hall effect measurements, that the  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloy system is one such system (Ivkov *et al* 1989). Therefore we have performed measurements of the thermopower in order to see whether the thermopower could support the applicability of the Faber–Ziman model to the case of  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloys. Accordingly, we have performed calculations based on the idea that has given good results for the  $\text{Ni}_x\text{P}_y\text{B}_{100-x-y}$  amorphous alloy system (Očko and Babić 1989).

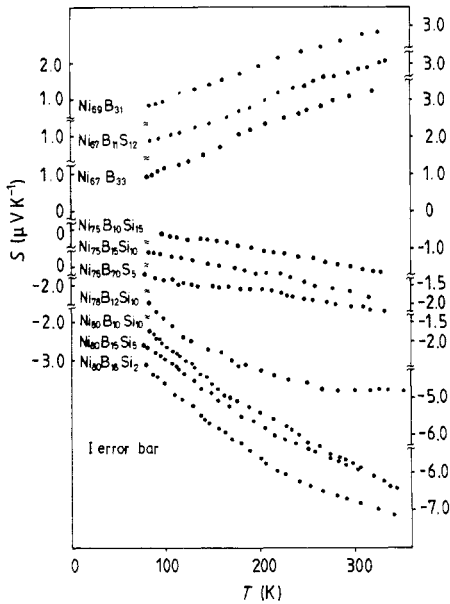
## 2. Experimental procedure and results

The samples were prepared at the Metglas Products Allied-Signal Inc., Parsippany, NJ. They were checked for amorphousness by x-ray diffraction and thermogravimetric measurements. The thermopower was measured relative to pure lead from liquid-nitrogen temperature up to room temperatures. The differential method was used. The temperature difference between the posts was measured by chromel–constantan thermocouples. The voltage connections were made by copper wires, having a diameter of  $30\ \mu\text{m}$ , fixed on the sample by silver paint. These copper wire connections were calibrated against a lead standard (Roberts 1977). The accuracy of the final thermopower result was within  $0.1\ \mu\text{V K}^{-1}$ .

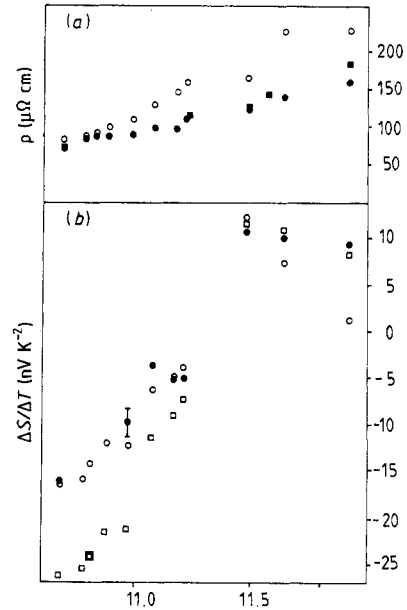
The results are shown in figure 1. The slopes of the thermopower  $S$  versus temperature  $T$  for  $\text{Ni}_{67}\text{B}_{33}$  and  $\text{Ni}_{61}\text{B}_{39}$  alloys are in agreement with those found in the literature (Varga *et al* 1984). As far as we know, there are no measurements of the thermopower of the other alloys containing Si. It is well known that it is not possible to obtain the amorphous phase of the  $\text{Ni}_x\text{B}_{100-x}$  amorphous alloy system in the concentration region 70–80 at. % Ni. Some fractions of Si enable the amorphous structure to be obtained even in this concentration region. This region is physically very important because it seems, according to the experimental results of the specific heat measurements (Kuentzler *et al* 1985), that in this region the Fermi level  $E_F$  crosses the d-band edge on the right-hand side, moving to larger values as the metalloid content increases. This crossover is dramatically reflected in the thermopower of the  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloy system. The thermopower is negative for  $x \geq 70$  and increases rapidly with decrease in  $x$ . For  $x < 67$  the thermopower is positive and decreases slightly as  $x$  decreases. Here we note that the normal Hall coefficient  $R_0$  does not exhibit such dramatic changes (Ivkov *et al* 1989). As one might expect for  $x \leq 75$ , the thermopower is small and more or less linear with temperature, extrapolating to a near-zero value when the temperature approaches zero. For  $x \geq 78$ , as in the case of the  $\text{Ni}_{81.5}\text{B}_{18.5-y}\text{P}_y$  amorphous alloy system for  $y \leq 3.7$  (Očko and Babić 1989), the thermopower is not linear and has rather large values. The main features of the temperature behaviour of the thermopower of the alloys in this concentration range are as follows:

- (i) There is a very steep increase up to about 100 K.
- (ii) For  $T > 100$  K the gradient  $\Delta S/\Delta T$  acquires smaller values and the thermopower is almost linear in temperature in some samples.
- (iii) Around room temperature the bending becomes pronounced again.

From such a temperature dependence of thermopower we conclude that we have two main contributions to the thermopower. In addition to the Ziman contribution, there is a significant contribution to the temperatures up to 100 K which becomes more



**Figure 1.** Thermopower for the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system versus temperature.



**Figure 2.** (a) Residual resistivities versus the number  $e/a$  of electrons per transition metal for the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system: ●, experimental values (Ivkov *et al* 1989); ■, experimental values (Varga *et al* 1984); ○, calculated values. (b) Rate  $\Delta S/\Delta T$  of change in the high-temperature thermopower and calculated values for  $\Delta S/\Delta T$  versus  $e/a$  for the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system: ●, experimental values; ○, calculated values (the choice for the derivatives of the phase shifts are explained in the text).

or less constant up to room temperature. At higher temperatures this contribution probably decreases when temperature increases.

The Hall effect measurements of  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system for low P concentration indicate this type of constant contribution in that temperature region, too (Ivkov *et al* 1990). As these concentrations are in the proximity of ferromagnetism, we therefore consider spin fluctuations to be a quite probable source of this contribution (Donald and Davies 1980). Therefore we ascribe the average gradient  $\Delta S/\Delta T$  of the thermopower in the temperature region between 100 and 200 K to the Ziman contribution to the thermopower. Such an extraction of a term proportional to temperature can be found in the literature (Sinha 1970, Cooper *et al* 1980, Somura and Maeda 1976, Očko and Babić 1989).

We note that the thermopower for  $x \leq 67$ , although linear, does not extrapolate to zero value. The probable reason for this effect is the electron-phonon mass enhancement (Gallagher and Greig 1982). The directly determined and estimated (for  $x \geq 78$ ) values of the linear terms  $(\Delta S/\Delta T)^{\text{exp}}$  representing the Ziman term are presented in figure 2(b) and table 1. We also note that, concerning the experimental results, the substitution of Si for B has much smaller effects on the thermopower than the substitution of P for B (Očko and Babić 1989).

**Table 1.** Experimental and calculated values of the transport coefficients of the Ni<sub>i</sub>B<sub>100-x-y</sub>Si<sub>y</sub> amorphous alloy system.  $e/a$  is the (largest possible) number of electrons per transition element for a given alloy, used only for the reason that the results could be plotted:  $e/a = |xZ_{Ni} + (100 - x - y)Z_B + yZ_{Si}|/x$ , where  $Z_{Ni} = 10$ ,  $Z_B = 3$  and  $Z_{Si} = 4$ .  $Z_c$  is the number of conduction electrons per atom,  $k_F$  the Fermi wavenumber,  $\rho$  the residual resistivity and  $\Delta S/\Delta T$  the rate of change in the thermopower. The theoretical values are calculated with two choices of derivatives of the phase shifts as described in the text.

Amount (at. %)		$Z_c$	$Z_c^{\text{exp}}$	$2k_F^{\text{exp}}$ ( $10^{10} \text{ m}^{-1}$ )	$2k_F$ ( $10^{10} \text{ m}^{-1}$ )	$\rho^{\text{exp}}$ ( $\mu\Omega \text{ cm}$ )	$\rho^{\text{th}}$ ( $\mu\Omega \text{ cm}$ )	$\frac{\rho^{\text{th}} - \rho^{\text{exp}}}{\rho^{\text{exp}}}$	$(\Delta S/\Delta T)^{\text{exp}}$ ( $\text{nV K}^{-2}$ )	$(\Delta S/\Delta T)^{\text{th}}$ ( $\text{nV K}^{-2}$ )	$\alpha^{\text{exp}}$ ( $10^{-4}$ )	$\alpha^{\text{th}}$ ( $10^{-4}$ )		
Ni	B	Si	$e/a$	$Z_c$	$Z_c^{\text{exp}}$	$2k_F^{\text{exp}}$ ( $10^{10} \text{ m}^{-1}$ )	$2k_F$ ( $10^{10} \text{ m}^{-1}$ )	$\rho^{\text{exp}}$ ( $\mu\Omega \text{ cm}$ )	$\rho^{\text{th}}$ ( $\mu\Omega \text{ cm}$ )	$\frac{\rho^{\text{th}} - \rho^{\text{exp}}}{\rho^{\text{exp}}}$	$(\Delta S/\Delta T)^{\text{exp}}$ ( $\text{nV K}^{-2}$ )	$(\Delta S/\Delta T)^{\text{th}}$ ( $\text{nV K}^{-2}$ )	$\alpha^{\text{exp}}$ ( $10^{-4}$ )	$\alpha^{\text{th}}$ ( $10^{-4}$ )
81.5	18.5	0	10.681	0.7449		2.5741	2.5741	70 <sup>a</sup>	82.7	0.18	-16.0	-16.41 <sup>c</sup> -26.36 <sup>d</sup>	+2.40 <sup>a</sup> +2.36 <sup>b</sup>	+10.1
80	18	2	10.775	0.7480	0.65 <sup>a</sup>	2.5786	2.5786	83 <sup>a</sup>	87.3	0.05	-17.0	-15.79 <sup>c</sup> -25.76 <sup>d</sup>	+1.80 <sup>a</sup>	+9.2
80	15	5	10.813	0.7540	0.71 <sup>a</sup>	2.5765	2.5765	87 <sup>a</sup>	91.6	0.05	-17.5	-14.46 <sup>c</sup> -24.36 <sup>d</sup>	+1.80 <sup>a</sup>	+8.4
80	10	10	10.875	0.7640	0.76 <sup>a</sup>	2.5731	2.5731	85 <sup>a</sup>	98.9	0.16	-16.0	-12.12 <sup>c</sup> -21.88 <sup>d</sup>	+1.70 <sup>a</sup>	+7.15
78	12	10	10.974	0.7824	0.89 <sup>a</sup>	2.72 <sup>a</sup>	2.6035	89 <sup>a</sup>	108.4	0.22	-9.8	-12.70 <sup>c</sup> -21.42 <sup>d</sup>	+1.35 <sup>a</sup>	+6.3
75	20	5	11.067	0.8800	0.82 <sup>a</sup>	2.68 <sup>a</sup>	2.7389	85 <sup>a</sup>	129.4	0.33	-4.0	-6.55 <sup>c</sup> -11.42 <sup>d</sup>	+1.20 <sup>a</sup>	+4.2
75	15	10	11.113	0.9000	0.91 <sup>a</sup>	2.76 <sup>a</sup>	2.7430	95 <sup>a</sup>	146.5	0.54	-5.2	-5.07 <sup>c</sup> -9.17 <sup>d</sup>	+1.10 <sup>a</sup>	+3.2
75	10	15	11.200	0.9200	0.93 <sup>a</sup>	2.76 <sup>a</sup>	2.7469	110 <sup>a</sup>	158.9	0.44	-5.0	-4.09 <sup>c</sup> -7.40 <sup>d</sup>	+1.00 <sup>a</sup>	+2.5
67	33	0	11.477	0.9900	1.13 <sup>a</sup>	3.10 <sup>a</sup>	2.9183	122 <sup>a</sup>	162.6	0.33	+10.4	+11.88 <sup>c</sup> +11.47 <sup>d</sup>	+0.22 <sup>a</sup> +0.12 <sup>b</sup>	+0.7
67	22	11	11.642	1.1000	1.21 <sup>a</sup>	3.12 <sup>a</sup>	2.9792	138 <sup>a</sup>	225.6	0.63	+9.9	+5.95 <sup>c</sup> +10.76 <sup>d</sup>	0.00 <sup>a</sup> -0.29 <sup>b</sup>	-0.2
61	39	0	11.920	1.1700	1.17 <sup>a</sup>	3.20 <sup>a</sup>	3.1266	160 <sup>a</sup>	227.2	0.42	+9.5	+1.15 <sup>c</sup> +7.87 <sup>d</sup>	-0.22 <sup>a</sup> -1.00 <sup>b</sup>	-3.7

<sup>a</sup> Experimental values from Ivkov *et al* (1989).

<sup>b</sup> Experimental values from Varga *et al* (1984).

<sup>c</sup>  $\partial\delta_2/\partial k = \partial\delta_{ij}/\partial k = 8 \times 10^{10} \text{ rad m}$ .

<sup>d</sup>  $\partial\delta_2/\partial k = 8 \times 10^{10} \text{ rad m}$  and  $\partial\delta_{ij}/\partial k = 2 \times 10^{10} \text{ rad m}$ .

### 3. Calculations

As we have already pointed out, the calculations of phase shifts taking into account the electronic structure of neutral atom (e.g.  $3d^9 4s^1$  for Ni) do not consider a very important effect: the effect of filling of the d band due to alloying with metalloids of a strong donor character. Therefore, by alloying with such metalloids, two effects may be recognised.

(i) The scattered electrons do not see just the simple electronic structure of a neutral atom.

(ii) The d character of the transition element is getting weaker.

The experimental conditions that we adhere to while performing the calculations are as follows.

(i) The specific heat measurements (Kuentzler *et al* 1985) show that the rigid-band model is appropriate for  $Ni_x B_{100-x-y} Si_y$  amorphous alloys. From these measurements one can conclude that, in this range of concentrations,  $E_F$  crosses the d-band edge on the right-hand side and that for  $x \leq 67$  the d band is full. These measurements enable us to make an estimation of the filling of the d band.

(ii) The Hall effect measurements (Ivkov *et al* 1989) show that for the  $Ni_x B_{100-x-y} Si_y$  amorphous alloy system the NFE model seems to be valid and so indicate that there is no anomaly in the dispersion relation for conducting electrons. These measurements enable us to make an estimation of the number of conduction electrons.

Within the framework of the Faber–Ziman theory the residual resistivity can be expressed in the form (Cote and Meisel 1979)

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

The thermopower is given by (Cote and Meisel 1979)

$$S = (\pi^2 k_B^2 T / 3 |e| E_F) (-2 + w + z) \quad (2)$$

with

$$w = [k_F / S_T(2k_F)] (\partial S_T / \partial k) |_{2k_F} \quad (2a)$$

and

$$z = (k_F / 2) \{ [\sin(2\delta_0) (\partial \delta_0 / \partial k) + 5 \sin(2\delta_2) (\partial \delta_2 / \partial k)] / (\sin^2 \delta_0 + 5 \sin^2 \delta_2) \} \quad (2b)$$

where  $\Omega_0$  is the volume per atom,  $k_F$  is the Fermi wavenumber, and  $m$  and  $e$  are the electronic mass and charge, respectively.  $c_{Ni}$  is the concentration of Ni. As is usually done in the case of alloys with a high transition-metal concentration, we ignore the direct influence of metalloids. However, as  $E_F$  approaches the edge of the 3d band, because of the alloying with metalloids one can expect that besides the  $\delta_2$  phase shift contribution, the contributions from  $\delta_0$  and  $\delta_1$  phase shifts become important as well. For simplicity we choose  $\delta_1 = 0$ . This choice will be discussed later. The relations above assume that the backward scattering is of main importance.

The temperature resistivity coefficient  $\alpha = (1/\rho)(\partial \rho / \partial T)$  is given by (Kaul *et al* 1986)

$$\begin{aligned} \alpha &= 2 \{ [1 - S_T(2k_F)] / S_T(2k_F) \} (\partial W / \partial T) \\ &= 8 \{ [1 - S_T(2k_F)] / S_T(2k_F) \} (3 \hbar^2 k_F^2 / 2 m_A k_B \Theta_D^2) \end{aligned} \quad (3)$$

where  $W(T)$  is the Debye–Waller factor,  $m_A$  is the atomic mass and  $\Theta_D$  is the Debye temperature.

The structure factor  $S(Q)$  has been calculated for each alloy from the Percus–Yevick model of dense random packing of hard spheres using the Goldsmith radii. A justification for the use of the Percus–Yevick model (taken from liquid alloys) lies in the fact that first peak of the  $S(Q)$  (inside which there is  $2k_F$ ) is almost the same shape for both liquid and amorphous alloys. The total packing fractions  $\eta$ , mean atomic volumes calculated in the usual manner (Ashcroft and Langreth 1967) and structure factors  $S(2k_F)$  taken at  $2k_F$  are given in table 2. The values of  $\eta$  are very close to those obtained by other workers for the similar amorphous alloy systems (Paja and Stobiecki 1984). Such calculated structure factors agree with the experimental findings (Dini *et al* 1986): when the metalloid content increases, the height of the first peak of  $S(Q)$  decreases.

The phase shifts commonly used have been calculated from the muffin-tin potential and the neutral atom wavefunctions were obtained. As we have discussed earlier, such a procedure does not take into account the important effect that occurs on alloying with metalloids of a strong donor character. Because of this we have rather made the following estimations of the phase shifts:

$$\delta_2 = (\pi/10)Z_d \quad \delta_0 = (\pi/2)Z_c \quad \delta_1 = 0$$

where  $Z_d$  is the number of d electrons per transition element and  $Z_c$  is the number of conduction electrons in a particular alloy. Such a choice of the phase shifts has been employed to explain the transport properties  $\alpha$ ,  $\rho$  and  $S$  of the  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloy system and has given good results (Očko and Babić 1989). The choice for  $\delta_2$  is consistent with that often found in the literature (Bell and Caplin 1975).  $\delta_0$  and  $\delta_1$  are chosen bearing in mind (Meisel and Cote 1983) that the phase shift is proportional to the number of electrons that fill corresponding states (similarly for the determination of the  $\delta_2$  phase shift). The choice  $\delta_1 = 0$  is used to simplify the calculations, but anyhow there are a relatively small number of p electrons in our alloys. However, here,  $Z_d$  is not the number of d electrons in the neutral atom. For the alloys with  $x \leq 67$ , we have taken  $Z_d = 10$  because there is experimental evidence that the d band is full owing to alloying with the metalloids (Kuentzler *et al* 1985). Accordingly, as the number of 3d and 4s electrons of Ni is 10, the conduction band of these alloys is filled by metalloid electrons only, and so, in this case, the number of the conduction electrons can be calculated from the expression  $Z_c = Z_M = Z_B(100 - x - y)/100 + Z_{\text{Si}}y/100$ , where  $Z_B$  and  $Z_{\text{Si}}$  are the numbers of electrons that boron and silicon give to the conduction band, respectively.

For the other alloys we have taken into account the effect of alloying, too. We have calculated  $Z_d$  according to the expression  $Z_d = 9.12 + Z_M(1 - p)/x$ . The number of conducting electrons is then calculated from  $Z_c = 0.88 + pZ_M$ . The numbers 0.88 and 9.12 represent the number of s and d electrons, respectively, for ‘amorphous Ni’ (Jaswal 1986, Očko and Babić 1989). Here  $p$  is the percentage of the number  $Z_M$  of the metalloid electrons that go into the conduction band of the alloy. Obviously, the metalloid electrons are shared between the conduction band and the d band. A plausible supposition is that  $p$  is proportional to the height of the conduction (s) band and inversely proportional to the height of the DOS (mainly determined by the d band). Unfortunately, there are no systematic specific heat measurements for alloys containing Si, and therefore we have made an estimation of the number of the metalloid electrons that go into the conduction band and into the d band, respectively, i.e. an estimation of  $p$  according to the available measurements of the specific heat of the  $\text{Ni}_x\text{B}_{100-x}$  and  $\text{Ni}_x\text{B}_{100-x-y}\text{Si}_y$  amorphous alloy systems (Kuentzler *et al* 1985).

**Table 2.** Selected and calculated quantities used as parameters in the calculations of transport properties within the framework of the Faber-Ziman theory (explanations are given in the text).

Amount (at. %)		$\Omega_0$ ( $10^{-38}$ m <sup>3</sup> )	$D$ (g cm <sup>-3</sup> )	$\eta$	$Z_B$	$Z_{Si}$	$P$ (%)	$Z_c$	$Z_d$	$S(2k_F)$	$w$	$z$	
Ni	B												Si
81.5	18.5	0	10.346	8.00	0.5566	1	2	15	0.74495	9.3129	0.1740	4.32	-6.57 <sup>a</sup> -9.14 <sup>b</sup>
80	18	2	10.334	7.95	0.5475	1	2	20	0.7480	9.6773	0.1909	4.22	-6.32 <sup>a</sup> -8.91 <sup>b</sup>
80	15	5	10.441	7.95	0.5425	1	2	20	0.7540	9.5769	0.2040	4.28	-6.03 <sup>a</sup> -8.59 <sup>b</sup>
80	10	10	10.622	7.95	0.5343	1	2	20	0.7640	9.4143	0.2269	4.38	-5.51 <sup>a</sup> -8.04 <sup>b</sup>
78	12	10	10.501	7.89	0.5438	1	3	30	0.7824	9.4072	0.2576	4.47	-5.84 <sup>a</sup> -8.17 <sup>b</sup>
75	20	5	10.146	7.79	0.5237	2	3	40	0.8800	9.5600	0.3783	5.23	-5.15 <sup>a</sup> -6.58 <sup>b</sup>
75	15	10	10.330	7.79	0.5154	2	3	40	0.9000	9.6000	0.4408	5.37	-4.86 <sup>a</sup> -6.07 <sup>b</sup>
75	10	15	10.514	7.79	0.5074	2	3	40	0.9200	9.6400	0.4925	5.37	-4.58 <sup>a</sup> -5.55 <sup>b</sup>
67	33	0	9.436	7.55	0.5024	3	4		0.9900	10	0.6760	5.77	+0.183 <sup>a</sup> +0.46 <sup>b</sup>
67	22	11	9.853	7.55	0.4835	3	4		1.1000	10	1.0900	5.95	-1.89 <sup>a</sup> +0.45 <sup>b</sup>
61	39	0	9.068	7.33	0.4763	3	4		1.1700	10	1.1415	5.86	-3.42 <sup>a</sup> -0.86 <sup>b</sup>

<sup>a</sup>  $\partial\delta_z/\partial k = \partial\delta_{0j}/\partial k = 8 \times 10^{10}$  rad m.

<sup>b</sup>  $\partial\delta_z/\partial k = 8 \times 10^{10}$  rad m and  $\partial\delta_{0j}/\partial k = 2 \times 10^{10}$  rad m.



One can conclude that  $Z_B$  and  $Z_{Si}$  must depend on the concentration ( $x$ ) of Ni. For  $Ni_{81.5}B_{18.5}$  amorphous alloy a good result has been obtained by taking  $Z_B = 1$  (Očko and Babić 1989) and for  $x \leq 67$  one has to take  $Z_B = 3$  (because the d band is fully occupied and only metalloid electrons fill the conduction band). So, one has to conclude that  $Z_B$  and  $Z_{Si}$  increase as  $x$  decreases. Such calculated values of  $Z_d$  (determined mainly by means of the specific heat measurements, which should be emphasised) and  $Z_c$ -values together with  $Z_B$ ,  $Z_{Si}$  and  $p$  are given in table 2. In table 1,  $Z_c$  is given again, together with  $2k_F$  calculated within the NFE model and with  $Z_c^{exp}$  and  $2k_F^{exp}$  obtained from the Hall effect measurements (Ivkov *et al* 1989). We can see that the agreement between  $Z_c$  and  $Z_c^{exp}$  is reasonable.

In table 2 the calculated values of  $w$  and  $z$  are presented as well. The densities of alloys are also included in table 2. Unfortunately, the majority of these values are extrapolated on the basis of the known data (Dini *et al* 1986, Cargil 1970).

In table 1 the experimental results of residual resistivities  $\rho^{exp}$ , the temperature coefficient  $\alpha^{exp}$  of resistivity found in the literature (Ivkov *et al* 1989, Varga *et al* 1984), and the thermopower gradient  $(\Delta S/\Delta T)^{exp}$  (this work) are compared with the calculated values of  $\rho$ ,  $\alpha$  and  $\Delta S/\Delta T$ .

The results for  $\rho$  and  $\Delta S/\Delta T$  are displayed in figures 2(a) and 2(b), respectively. The experimental values are represented by the full circles and full squares ( $\rho$  of Varga *et al* (1984)). The open symbols represent the corresponding calculated values.  $\Theta_D = 300$  K has been taken for all alloys in the calculations of the value of  $\alpha$ . In figure 2, two choices for the derivatives of the phase shifts with respect to  $k$  have been taken in the calculations: open circles represent  $\partial \delta_2/\partial k = \partial \delta_0/\partial k = 8 \times 10^{10}$  rad m, as in the case of  $Ni_{81.5}B_{18.5-y}P_y$  (Očko and Babić 1989); for the open squares,  $\partial \delta_0/\partial k$  is taken to be four times smaller and  $\partial \delta_2/\partial k = 8 \times 10^{10}$  rad m.

#### 4. Discussion and conclusion

At first glance, one can see that the calculations have given the right concentration dependence of all transport properties considered ( $\rho$ ,  $\alpha$  and  $\Delta S/\Delta T$ ) for the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system.

The calculated values of residual resistivity  $\rho$  for alloys with a large metalloid content are larger than the experimental values. The following reasons might explain such a discrepancy.

(i) Here we are in the region of a very rapid change in the structure factor and even small uncertainties in various parameters (density, diameters of atoms,  $k_F$  and so on) may yield considerably different results.

(ii) Also, there is an enhanced number of p electrons but to all of them we have ascribed an s-like character.

(iii) Finally, when  $\rho$  exceeds  $150 \mu\Omega$  cm, i.e. when the mean free path of the electron is about the mean atomic distance, either the use of the Boltzmann equation is questionable, or this effect has to be taken into consideration.

The possible effect of weak localisation which becomes important for high-resistivity alloys has been discussed in a previous paper (Očko and Babić 1989).

The theoretical values of the room-temperature coefficient  $\alpha$  of resistivity have the right concentration dependence. Moreover, a change in sign takes place about the correct concentration. However, for the lower metalloid concentrations, calculated

values of  $\alpha$  are very much larger than the experimental values. The reason might lie in the crudeness of the theoretical derivation of equation (3).

The Ziman contribution to the thermopower  $S$  is explained by the interplay of  $w$  which gives the influence of scattering on disorder and  $z$  which gives the contribution to  $S$  due to electronic structure. According to our results, by increasing the metalloid content,  $E_F$  (and/or  $k_F$ ) becomes larger, moving from the region where  $z$  dominates to the region where  $w$  dominates, i.e. from the region where the DOS dominates, giving a negative thermopower, to the region where the structure factor dominates, giving a positive thermopower. When d states are not full,  $z$  alone gives negative values of  $S$  because it is extracted from the DOS. This is the reason why we can get a large negative value of  $S$  within the Ziman model. We suggest that because of the shape of the DOS of the late transition elements (Ni, Pt and Pd) they have a large negative value of  $S$ . There has been a suggestion (Varga *et al* 1984) that, within the Ziman model, only alloys with a high metalloid concentration could be explained.

The thermopower is calculated with two different choices of parameters for the derivatives of the phase shifts which are described above (figure 2) and, although there is a great difference between these choices, the overall concentration dependence is correct for both choices.

One more fact is evident: namely, in order to obtain agreement between the calculated number of conduction electrons and the value determined from the Hall experiments, it has to be assumed that the number  $Z_{Si}$  of electrons that silicon gives is not very much greater than the number  $Z_B$  that boron donates. This is reflected in the calculation of thermopower and gives the experimentally observed results; the thermopower does not change very much by substituting Si for B. The situation in  $Ni_{81.5}B_{18.5-y}P_y$  is quite different. There  $Z_P/Z_B = 3$  and the thermopower undergoes a significant change upon substitution of P for B (Očko and Babić 1989).

As the conclusion, we note that the calculation within the Faber–Ziman model of the transport properties  $\rho$ ,  $\alpha$  and  $S$ , taking the plausible premises and extracting the parameters from the measurements in the same way as has been done for  $Ni_{81.5}B_{18.5-y}P_y$ , has given a good concentration dependence for the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system, too, in the whole concentration region considered. Accordingly, one may conclude that the Ziman theory is capable of giving a possible explanation of the transport properties of the  $Ni_xB_{100-x-y}Si_y$  amorphous alloy system.

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