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THERMOPOWER OF $Ni_{81.5}B_{18.5-y}P_y$ AMORPHOUS ALLOYS

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The thermopower of the amorphous nonmagnetic alloy system $Ni_{81.5}B_{18.5-y}P_y$ (y=0, 1.8, 3.7, 7.4, 13, 16.8, 18.5 at %P) has been measured as a function of temperature between 77 and 350 K. The main features of the thermopower behaviour are as follows: i) the thermopower is positive for y > 13 at %P; ii) linear within the whole temperature range for y > 7.4 %P; iii) nonlinear (similar to that of a ferromagnet in the low temperature region); iv) for y=0 at %P and y=1.8 at %P the thermopower reaches unexpectedly large negative values, even larger than those of the amorphous ferromagnets.

The thermopower results together with the earlier results for the residual resistivity and the temperature coefficient of resistivity /1/ are discussed within the framework of the extended Ziman theory.

The applicability of the diffraction model of the transport properties for ideal crystalline metals and for liquid metals is well established. This model also gives a good description of crystalline and amorphous alloys /2/ not containing transition metals. Several reasons for the inefficiency of the diffraction model in the case of transitional alloys have been discussed in the literature but one reason which shows up when analysing the expression for resistivity is often ignored. Here is the expression for calculating the residual resistivity in the Ziman theory:

$$\rho = \frac{3\pi\Omega}{4e^2\hbar v_F k_F^4} \int_0^{2k_F} dQ Q^3 S(Q) |t(Q,E_F)|^2$$

where S(Q) is the structure factor, Ω atomic volume, e the charge of electron, v_F the Fermi velocity, k_F is the Fermi wave number and

$$t(Q,E_F) = \frac{-2\pi\hbar}{\Omega m(2mE_F)^{1/2}} \sum_{\ell}(2\ell+1) \sin\delta_\ell(E_F) e^{i\delta_\ell(E_F)} P_\ell(\cos\theta)$$

is the t matrices, E_F is the Fermi energy, P_ℓ is the Legendre polynomial and δ_ℓ is the phase shifts. The usual phase shifts one calculates /2/ taking the electronic structure of Ni for example: $3d^9 4s^1$. But there are experimental evidences that alloying changes the electronic structure /3,4/. Therefore δ_ℓ calculated on the above mentioned assumptions are not physically justified.

In order to include the change of the d state on alloying into the calculations one has to find a suitable alloy system. In our opinion $Ni_{81.5}B_{18.5-y}P_y$ amorphous alloys are such a system, because they are nonmagnetic /3/ and their densities of states are known from the specific heat measurements /4/. Since we were aware that resistivity results /1/ alone might lead to erroneous conclusions we also performed the thermopower measurements.

The samples were produced and checked at CRIP, Budapest. The thermopower was measured relative to pure lead from 77 up to 350 K. The differential method was used. The connections were made with the 30 μm in diameter Cu wires fixed on the sample by the silver-paint. Temperature was measured by chromel-constantan thermocouples. The absolute thermopower of sample is obtained by substracting the absolute thermopower of the lead standard /5/ from the measured thermopower. The accuracy of the thermopower values is within $\pm$ 0.1 μVK^{-1}.

The results are shown in Fig.1. They are in excellent agreement with the available results of the other authors /6,7/. The main features of the thermopower behaviour are already listed in the abstract. The amount and temperature dependence of the thermopower for $y > 7.5$ at %P is consistent with that expected from the Ziman theory and our calculations undoubtedly confirm that. The problems arise for the concentrations $y < 3.7$ at %P. Some possible explanations of a large negative thermopower of the boron rich alloys are listed below.

As the resistivity decreases the electronic mean free path increases and than dividing electrons to s and d has a sense. Than the Mott theory can be applied, which might lead to high thermopower values. The investigations /3,4/ show that the electronic structure of our system is Pd like and Pd has a large negative thermopower well explained by the Mott theory. Indeed, there is a suggestion /6/ that the thermopower of NiBP alloys over the whole concentration range can be explained by the Mott theory. Hoever to explain the positive thermopower with the Mott theory, there has to be a minimum in the density of states (DOS) at the Fermi level. The DOS of our alloys smoothly varies on the alloying, which in terms of the rigid band model (used in explanation of some properties /3,4/) means a smooth variation of the DOS with energy. Hence it is hard to believe that a minimum in the DOS exists in NiBP alloys.

Phonon drag contribution to the thermopower is expected to be absent in the amorphous solid. However on the boron rich side of the system

resistivity is smaller leading to longer wavelenghts of the electrons and hence to enhanced phonon-electron scattering possibly more important than the scattering of phonons by disorder. The reduction of the thermopower in a similar $Ni_{80}B_{18}Si_2$ matrix caused by a small amount of Fe might support the phonon drag contribution in our alloy too. Of course, a giant thermopower exists in NiBSi alloys, too. A similar reduction of the phonon drag contribution by Fe impurities is also observed in crystalline alloys.

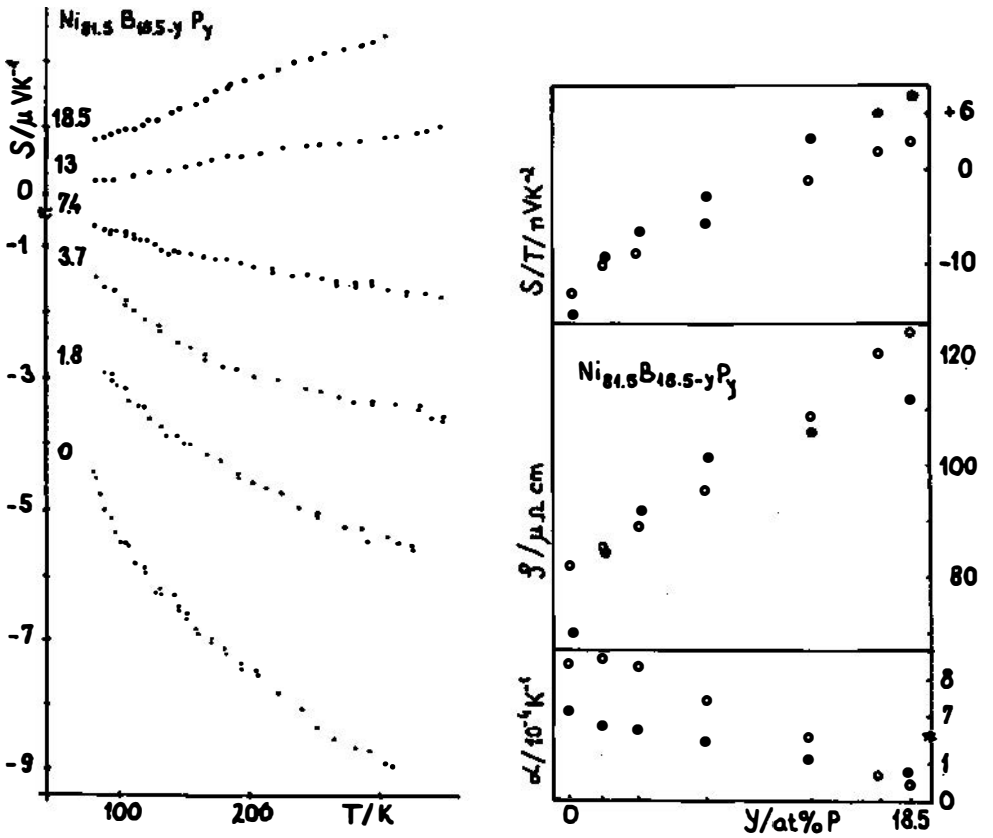

Fig. 1. Thermopower of amorphous $Ni_{81.5}B_{18.5-y}P_y$ alloys vs temperature.

Fig. 2. Experimental (.) and theoretical (o) results of the rate of change of the high temperature thermopower (S/T), residual resistivity (ρ), the temperature coefficient of resistivity (α).

As a "spoorious effect" we might mention the eventual ferromagnetic cluster which might behave like a giant moments giving a large thermopower. (Note on the boron rich side we are in the critical concentration region for the formation of the amorphous state. As the last possible explanation of a giant thermopower we mention the electron-phonon mass enhancement. However it is hard to believe it gives such a large negative contribution. This effect might however be the real reason why the high temperature thermopower for $y > 13$ at %P does not extrapolate to zero.

At this stage, we cannot tell conclusively what is the origin of a giant thermopower in some of our alloys. But all the mentioned mechanisms are not so important at higher. Hence the rate of change of the thermopower with the temperature for $T > 80$ K reflects mainly the diffusion thermopower which we shall try to explain within the framework of the Ziman theory. The detailed explanation of the performed calculations for the residual resistivity, the temperature coefficient of resistivity and the thermopower will be given elsewhere /8/. Here we only show the results of the theoretical calculations together with experimental results. There can be seen a surprisingly good agreement between the theoretical and experimental results. We note for the residual resistivity that the agreement between our calculations and experimental results will be even better. The only discrepancy is for the temperature coefficient of resistivity, but the concentration dependence of the theoretical and experimental results is the same. These results indicate that the Ziman theory can be applicable for the amorphous $Ni_{81.5}B_{18.5-y}P_y$ alloys.

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