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The Peculiarities of the Electronic Structure of NiPdP Based Amorphous Alloys

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The density of the electronic states for the Ni-Pd-P-based amorphous alloys has been calculated using an extension of the s-d band model in the coherent potential approximation in the case of a topological disordering. The calculated density of states is shown to be in a good agreement with the data of optical experiments. The conductivity properties are shown to be caused by the involving of the Anderson's localized electronic states into the kinetic process.

Keywords: amorphous alloys, electronic structure.

Introduction

Amorphous metallic alloys are of interest in studying physical properties of disordered systems. Recently, many theoretical and experimental works were devoted to the problem of studying the electronic structure of these materials. But instability of amorphous metallic alloy restricts the possibilities of their applications. The magnetic properties and thermal stability of amorphous alloys are known to be highly sensitive to the presence of non-metallic glass formers [2]. It is, thus, necessary to elucidate the factors affecting these properties. In this context, one of the important problems consists in the determination of the electronic structures of amorphous metallic alloys and their relationships to the structural stability. Much theoretical and experimental efforts have recently been devoted to the investigation of electronic structures of these materials. Solutions to this problem would allow producing stable amorphous metallic alloys with useful applications.

Here we present the results of calculation of the densities of states in the Ni-Pd-P based amorphous alloys. The calculations were performed by extending the s-d band model of coherent-potential approximation to the case of alloys d topological disordering.

I. Results and discussion

It is necessary to note that the simultaneous analysis of the physical properties and the peculiarities of the electronic structure of the Ni-based amorphous alloys at their chemical composition changing permits not only to extend our knowledge about the nature of the disordered

materials but also gives the possibility to create new amorphous alloys with the improved level of the service characteristics.

The modified coherent-potential method [3] has been applied to calculate the parameters of the electronic structure. Since the coordination number of transition metal-transition metal (TM-TM) pair in the Ni-based amorphous alloys is close to 12 [4] we used the electronic spectrum of fcc-lattice in the tight-binding approach as a zero approximation. The averaging has been carried out according to the radial distribution function g(r), which was obtained by the XRD experiments [5]. The Harrison's parameterization was used to calculate the hopping integrals [6].

Fig. 1 displays the electronic spectrum n(E) of amorphous Ni obtained by the mentioned approach. The main feature of this spectrum is the presence of the main peak, which is formed by 3d-states. The width of this peak is ~ 4 eV. The Fermi level E_F, which is marked by a vertical line at the figure is located essentially higher than the maximum of the main peak in a region of n(E) sharp decreasing. According to Ref. [7] one can mention the following peculiarities of the electronic spectra of the Ni-based amorphous alloys, which was obtained by the optical experiments: the presence of the well-defined peak with the half-width ~ 2.5 eV, which is located down from the Fermi level on 0.5-0.8 eV. These experimental results are in a good agreement with our speculations. This permits us to conclude the validity of the proposed method of calculation.

The next stage of our investigations is the exposure of the correlation between the parameters of the electronic structure and the physical properties of the Ni-Pd-P based amorphous alloys. Our approach is originated
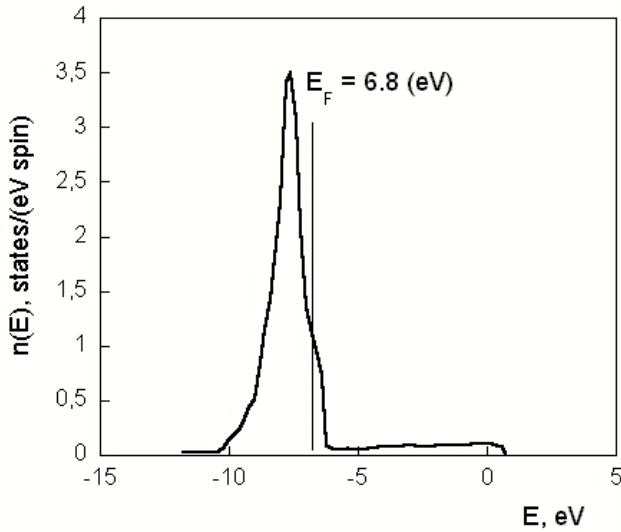
Fig. 1. The density of electronic states n(E) calculated for amorphous Ni.

from the Anderson's model of the localization [8]. According to that model the presence of the topological disordering leads to the formation at the edges of the energy bands the areas of the localized states, which are separated from the delocalized ones by the mobility edge E_c (Fig. 2). In this case the behaviour of the kinetic properties, i.e. the temperature dependencies of the

resistively depends on the Fermi level E_F location with respect to E_c. If the Fermi level is places in the area of the extended states one can observe the positive values of the temperature coefficient of resistivity (TCR) α and close to the linear increase of the resistivity with temperature. If E_F is located in the area of the localized states the temperature dependence of the resistivity is in a good agreement with the exponential function and TCR is getting the negative values. When the Fermi level is close to E_c both localized and delocalized electronic states give a contribution into conductivity. In this case the changing of the components' content influences essentially on the temperature dependence of resistivity. As it was shown in Refs. [9] (for the Ti-Cu and Ti-Ni-based amorphous alloys and the Ni-based metallic glasses (MGs), respectively) it takes place because of the Fermi level of such MGs is located higher than the localized states area. One can predict that the same situation will take place in the Ni-Pd based amorphous alloys.

We considered three main types of atomic configurations for the Ni-Pd-P-based MGs: $NiPd_2$, Ni_3Pd_2 and NiPd. The chemical compositions, TCR values and crystallization temperature T_x [10] are listed in Table.

Fig. 3 displays the calculated density of electronic states for different atomic configurations of Ni-Pd. It is seen that the calculated band structure for all atomic configuration is nearly the same. The Fermi level is
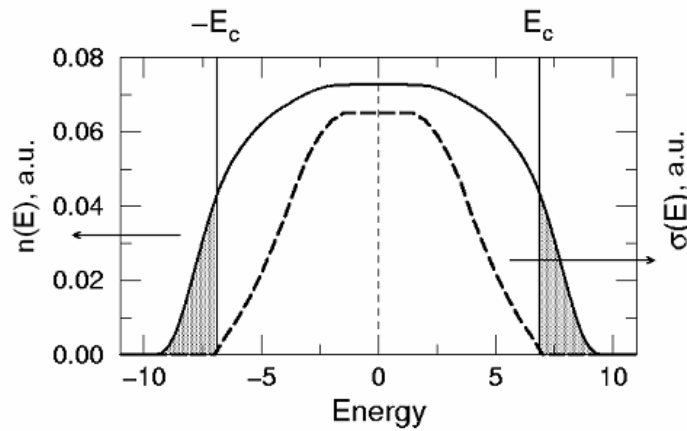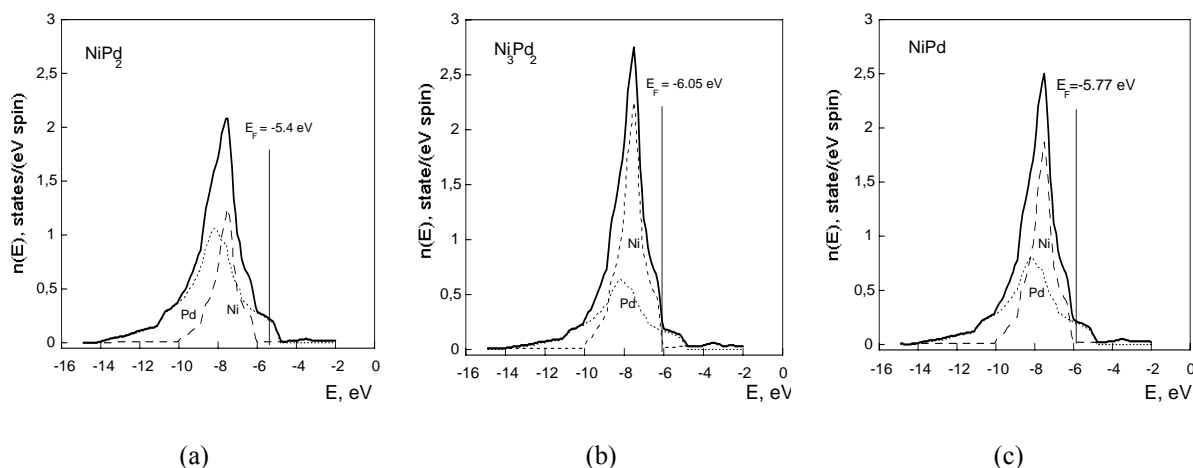

Fig. 2. The model electronic band and conductivity, gray denotes the localized electronic state regions [4].

Table

Samples' identification, the temperature coefficient of resistivity and the crystallization temperature

Composition	Type of atomic configuration	$\alpha \cdot 10^{-5}$, K^{-1}	T_x, K
$Ni_{28}Pd_{58}P_{14}$ $Ni_{32}Pd_{52}P_{16}$	$NiPd_2$	12.4 11.8	590 610
$Ni_{47}Pd_{37}P_{16}$ $Ni_{46}Pd_{36}P_{18}$ $Ni_{46}Pd_{31}P_{23}$	Ni_3Pd_2	10.6 10.7 -0.1	600 600 590
$Ni_{40}Pd_{40}P_{20}$ $Ni_{42}Pd_{42}P_{16}$	NiPd	5.4 10.3	640 610

Fig. 3. The density of electronic states n(E) calculated for amorphous NiPd$_2$ (a), Ni$_3$Pd$_2$ (b) and NiPd (c). Vertical lines mark the position of the Fermi level.

located at higher energies with respect to the main peak. It means that E_F is placed in the area of the extended electronic states slightly lower than the mobility edge E_c.

It is seen from the Table that the TCR values are decreasing with P content increasing and becomes negative at P content 23 at %. Such behaviour can be explained taking into account the role of localized and extended states in the formation of kinetic characteristics. According to the model of charge transfer P atoms give into Ni valence band approximately 2 electrons, but they do not change essentially its shape [5]. So, at P content increasing the quantity of valence electrons in d-band of Ni-Pd increases and the Fermi level is shifted to the right – closer to the edge of 3d-band. Thus, P atoms are donors of electrons. One can conclude that if E_F of Ni-Pd amorphous compound is located in the area of the extended states the P content increasing will lead to the E_F shifting into the area of the localized states. The fact that TCR is changed is a certain manner not only with P content changing but also with TM content changing is noteworthy. So, we can admit, analyzing the experimental result that α specifies the tendency for decreasing with Ni content increasing. It is necessary to note that the TCR change is less clearly defined with substitution of Ni for PD in NI-Pd-P alloys than with

substitution of Ni for Pt in Ni-Pt-P alloys [10]. Evidently, it is connected with the position of Pt states at higher energies than Pd d-states.

Conclusions

It is shown that the suggested approach for calculation of the electronic spectrum of the Ni-Pd-P amorphous alloys is efficient. The peculiarities of the electronic spectrum have been discussed. The conductivity properties are shown to be caused by the involving of the Anderson's localized electronic states into the kinetic process. The role of P atoms in the kinetic properties has been analyzed.

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[1] K Suzuki, H. Fujimori and K. Hashimoto. *Amorphous metals*. Metallurgy, Moscow. 328 p. (1987) (in Russian).

[2] *Glassy metals II*. Eds.: H.Beck, H.J.Guntherodt. Springer-Verlag, Berlin, Heidelberg, N. Y. Tokyo, 356 p.(1983)

[3] O.I. Nakonechna, I.V. Plyushchay, M.I. Zakharenko, R. Hasegawa. Electronic structure and stability of metallic galsses on the basis of transition metals.//Physics of Metals and Metallogr., **95** (1), pp. 1-5 (2003).

[4] *Glassy metals*: Ed. by R. Hasegawa. Boca Raton, Fl: CRC Press. pp. 65-108 (1983).

[5] V.V. Nemoshkalenko, A.V. Romanova, et. al., *Amorphous metallic alloys*. Kyiv, Nauk. Dumka, 248 c. (1987). (in Russian).

[6] Harrison W.A., *Electronic Structure and the Properties of Solids*, San Francisco: Freeman, (1980).

[7] N.G. Babich, L.V. Poperenko, I.A. Shaikevich, N.I. Zakharenko, The factors of thermostability of the Ni-based amorphous alloys //*Optical Mater*., **4** , pp. 617-621 (1995).

[8] M.U. Belyi, L.V. Poperenko, I.A. Shaikevich, Ellipsometric Spectroscopy of Valence States in Amorphous Metallic Alloys // *Thisn Solid Films*, **234**, pp. 542-544 (1993).

[9]   O.I. Nakonechna, I.V. Plyushchay, M.P. Semen'ko, M.I. Zakharenko, Electrical resistivity and electronic structure of Ti-Ni and Ti-Cu based amorphous metallic alloys // *Phys. Metals and Metallogr*. **90** (5), pp. 439-444 (2000).

[10] M. Babich, O. Nakonechna, M. Semen'ko, M. Zakharenko, G. Yeremenko, A.R. Yavari, Correlation between resistivity characteristics and electronic structure parameters of the Ni-Pd-P amorphous alloys// *Mat. REs. Soc. Symp. Proc*. **644** pp. L12.1.1-L12.1.6. (2001).

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Особливості електронної структури аморфних сплавів NiPdP

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Модифікованим методом когерентного потенціалу з урахуванням топологічного безладу розраховано електронний спектр аморфних сплавів NiPdP. Виявлено, що одержані дані добре корелюють з експериментом. Показано, що локалізовані електронні стани відіграють визначальну роль у формуванні кінетичних характеристик, зокрема, питомого опору.