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EFFECT OF ATOMIC SUBSTITUTIONS ON THE ELECTRONIC STRUCTURE OF $Pt_{1-x}Ni_xMnSb$ ALLOYS ($x = 0.0 \div 1.0$)

Using zone calculations in the FLAPW (the full-potential linearized augmented-plane-waves) model, the information on the energy, charge, and spin characteristics of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) is obtained. It is established that, with an increase in the concentration of nickel atoms in $Pt_{1-x}Ni_xMnSb$ alloys, the interatomic space density of electrons decreases, covalent bonds weaken, and the cohesive energies of the alloys decrease. The dominant contributions to the formation of magnetic moments in $Pt_{1-x}Ni_xMnSb$ alloys are made by 3d electrons of manganese atoms. In alloys with $x \geq 0.50$, the complete polarization of Fermi electrons is registered, which converts these alloys to a half-metallic state.

K e y w o r d s: bandstructure calculations, Heusler alloys, bandstructure, magnetic moments, polarized bandstructure state, spintronics.

1. Introduction

A variety of materials with complex crystal structures that exhibit unusual electronic and magnetic properties has always attracted a considerable attention of theorists and experimenters for the purpose of using these unconventional properties in possible practical applications. One such group of materials which is being actively investigated are the Heusler compounds. The parent Heusler compounds, the so-called the full-Heusler phases (L2₁-structures), have the general formula X₂YZ, where X and Y are transition metals, and Z is an sp-valent elements. The half-Heusler phases (C1ᵦ-structures) have the same structure, except that one of the sites occupied by the X atom in the parent compound is empty, giving the general formula XYZ [1]. These phases have [2–5] a complex of magnetic, kinetic, optical, magneto-optical, superconducting, thermoelectric, and other important properties. In the system of compounds under discussion, it is possible to implement topological insulators and the so-called half-metallic state of a solid with a completely uncompensated spin density

of band electrons at the Fermi level – an important property necessary in technologies for creating materials for spintronics devices.

In 1983, de Groot and co-workers [6] discovered by *ab initio* calculations that one of the half-Heusler alloys, NiMnSb, is half-metallic, i.e., the minority band has a band gap at the Fermi level. This conclusion is confirmed in a series of other works – see, for example, reviews [7, 8]. Cl₀,-type Heusler compounds have attracted much attention due to the discovery of the very large Kerr effect in PtMnSb [9]. This large effect, a maximum of 1.3° at 1.7 eV in the room-temperature Kerr-rotation spectrum, has been attributed to the unusual electronic structure of this material. Long-standing calculations [6] of the zone structure showed that PtMnSb belongs to the class of the so-called half-metallic materials, but there is no convincing experimental evidence for this fact in the literature. Moreover, in the calculations [7, 8], the value of 66.5% was obtained for the polarization of valence electrons at the Fermi level in the PtMnSb compound.

The sequential transition of PtMnSb → NiMnSb was studied in [10, 11] using the system of solid solutions $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$). It is established here that this transition does not lead to

a change in the symmetry of the crystal lattices of solutions. Using X-ray diffraction, the parameters of their cubic lattices were determined, and the magnetic, temperature, and magneto-optical characteristics were measured.

Outside of the cited works, a number of comparative characteristics of the electronic structure of these alloys have not been studied. There was no complete information about their energy characteristics, the spin and charge states of atoms, the nature of interatomic chemical bonds, and the structure of valence bands and conduction bands. The present work is devoted to finding the solutions of these problems.

2. Methodology of the Calculations

The "parent" half-Heusler alloys PtMnSb and NiMnSb crystallize in the cubic syngony with the space group F-43m (№216) [12]. As already mentioned, experimental studies of the alloys with mixed atomic composition $Pt_{1-x}Ni_xMnSb$ [10, 11] did not reveal a significant rearrangement of the symmetry of their crystal lattices. To simplify the calculation procedure in this paper, the positions of the component-atoms of the $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) are set using the symmetry operations of a simple cubic lattice P. The correctness of this approach on the example of the study of half-Heusler phases is proved by us in [13, 14].

Band calculations were performed by the LAPW method [15] with a gradient approximation of the electron density (GGA-generalized gradient approximation) in the form given in [16]. A spin-polarized version of this method was used to calculate the characteristics of the electronic structure [17]. The parameters a of the cubic lattices of the $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) required for the calculations are borrowed from the experimental data obtained in [10]. The radii (Rmt) of the MT (muffin-tin) – atomic spheres were chosen from the consideration of minimizing the size of the inter-sphere region in the NiMnSb alloy, which has the smallest unit cell volume. For all alloys and all the atoms in them, these radii were 2.18 Bohr radius (1 Bohr radius = $= 5.2918 \times 10^{-11}$ m). When calculating the characteristics of the electronic structure of all alloys, 172 points in the irreducible parts of their Brillouin zones were used. APW + lo bases are used to approximate the wave functions of the 3d electrons of all

atoms, and LAPW bases are used for the wave functions of the remaining valence electrons. The size of the basis set was determined by setting the product $R_{mt}K_{max} = 7.0$ (K_{max} is the maximum value of the inverse lattice vector). When selecting the maximum orbital quantum number for partial waves inside the MT spheres, the value $l = 10$ is used. The non-muffin-tin matrix elements were calculated using $l = 4$. The convergence parameters for calculating the energies and charges at the final iteration of the calculations were 0.0001 Rydberg and 0.0001 e⁻ (electron charge), respectively. These parameters determine the accuracy of determining the energy and charge characteristics of the alloys under study.

The binding energies (cohesion energies) were calculated as the differences between the total energies of the atoms forming the unit cells of the alloys themselves, and the sum of the total energies of their constituent atoms, separated from each other by "infinity". They were determined in accordance with the recommendations [18].

The degree of polarization (P) of Fermi electrons was determined by the formula [19]:

$$P = \frac{D_\uparrow(E_F) - D_\downarrow(E_F)}{D_\uparrow(E_F) + D_\downarrow(E_F)}, \tag{1}$$

where $D_\uparrow(E_F)$ $D_\downarrow(E_F)$ are the total electron state densities at the Fermi level (E_F) with the spin directions up and down, respectively.

3. Results and Discussion

In works [13, 14, 20], it was found that the chemical composition and atomic disorderings corelationally affect the interatomic bond energies, the degree of their covalence, and the parameters of the unit cells in half-Heusler alloys. Similar dependences, as indicated in (Fig. 1), are also characteristic of $Pt_{1-x}Ni_xMnSb$ ($x = 0.0 \div 1.0$) alloys. It can be seen that the drop in the charge density in the interatomic region is accompanied by a decrease in the binding energies of the atoms in the alloys under study. Based on this and the theory of valences [21], the following conclusion can be formulated: a decrease in the spatial density of electrons in interatomic regions with an increase in the concentration of nickel atoms in $Pt_{1-x}Ni_xMnSb$ alloys leads to the loosening of chemical interatomic bonds. In turn, this same reason leads to a concomitant decrease in the cohesive energies of atoms in

these alloys. The latter fact may indicate a loss of the thermodynamic stability of $Pt_{1-x}Ni_xMnSb$ alloys with an increase in the nickel concentrations in them.

The concentration dependence of the parameters a of the crystal lattices correlates with the charges of the atoms in the alloys. The quantitative values of these charges and their dependences on the concentrations of nickel atoms in the alloys are shown in (Fig. 2). It can be seen that, with increasing nickel concentration in $Pt_{1-x}Ni_xMnSb$ alloys, the number of electrons in the atomic spheres of metals increases monotonically. Note that the transition to alloys with a maximum nickel concentration is accompanied by a small increase in the number of electrons on the Pt and Sb atoms by 0.09 and 0.06 percent, respectively. Slightly larger values in the variations of these charges are characteristic of the Ni and Mn atoms – 0.41 and 0.12 percent, respectively. A possible reason for such variations in Q is an increase in the degree of delocalization of valence electrons in a number of atoms Pt, Sb, and Ni, Mn – the reaction to a sequential decrease in the charges of the nuclei of these elements. In particular, the increased delocalization of the valence electrons of nickel and manganese atoms provides an increased dynamics of the formation of their chemical bonds with the surrounding atoms and, as a result, leads to large changes in the Q values. The primary cause of these changes in the charge states of atoms is obviously a reduction in the parameter *a* of the crystal lattices of alloys with an increase in nickel concentrations in them (Fig. 2, right panel).

This dependence of the parameter a on the nickel concentration in $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) is due to the reduced atomic radius of nickel, equal to 1.24 Å, compared with the same for platinum atoms, equal to 1.39 Å [22]. As a consequence of this and the already mentioned "aspiration" of alloys to dense atomic packages (*fcc-structures*), it should inevitably lead to a decrease in the values of parameter a with an increase in the concentration of nickel in the alloys. If the atomic radii of the substituting components exceed the size of the platinum atoms, then, according to the above considerations, in a series of solid solutions, the parameter a should increase with the concentrations of embedded atoms. Indeed, such a pattern can be seen for a series of $Pt_{1-x}Au_xMnSb$ alloys ($x = 0.0 \div 1.0$) [11] for which the atomic radius of gold is 1.44 Å [22]. Another confirmation of the above assumptions is the course of the dependence $a(x)$ in the
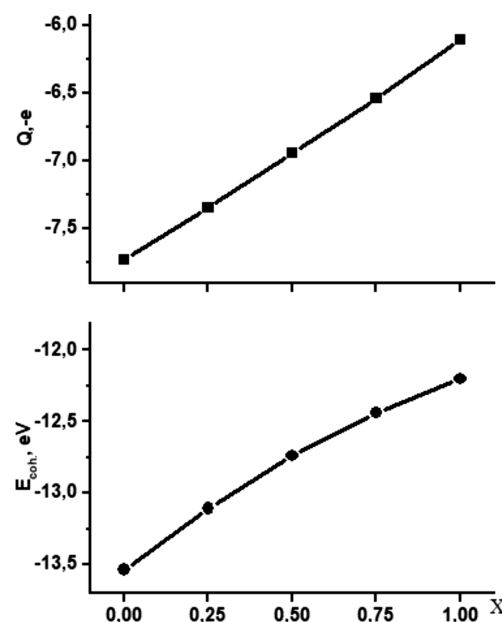
Fig. 1. Interatomic charges (Q, e-electron charge) and binding energies ($E_{coh.}$) of atoms in $Pt_{1-x}Ni_xMnSb$ ($x = 0.0 \div 1.0$)

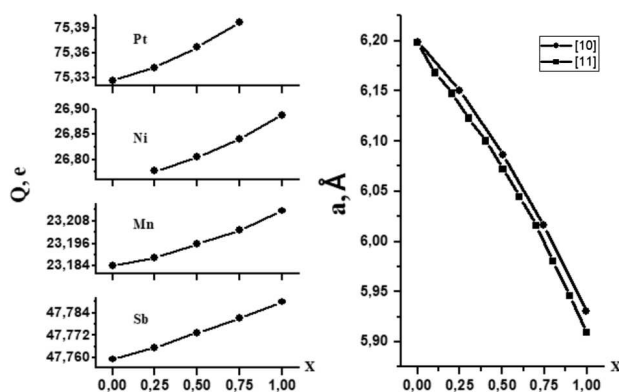**Fig. 2.** Concentration dependences of atomic charges (Q, e-electron charge) and parameters (a) of conventional cells of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$)

$Pt_{1-x}Cu_xMnSb$ series of alloys ($x = 0.0 \div 1.0$) [11]: here, at an atomic radius of 1.28 Å of copper [22], a decreasing course of the curve $a(x)$ at $x \to 1.0$ is observed, as in alloys with nickel. It should be noted that the current values of $a(x)$ in copper alloys exceed those for nickel alloys [11]. The latter circumstance is explained by a somewhat larger radius of copper atoms.

Additional information about the nature of chemical bonds in the studied alloys can be obtained
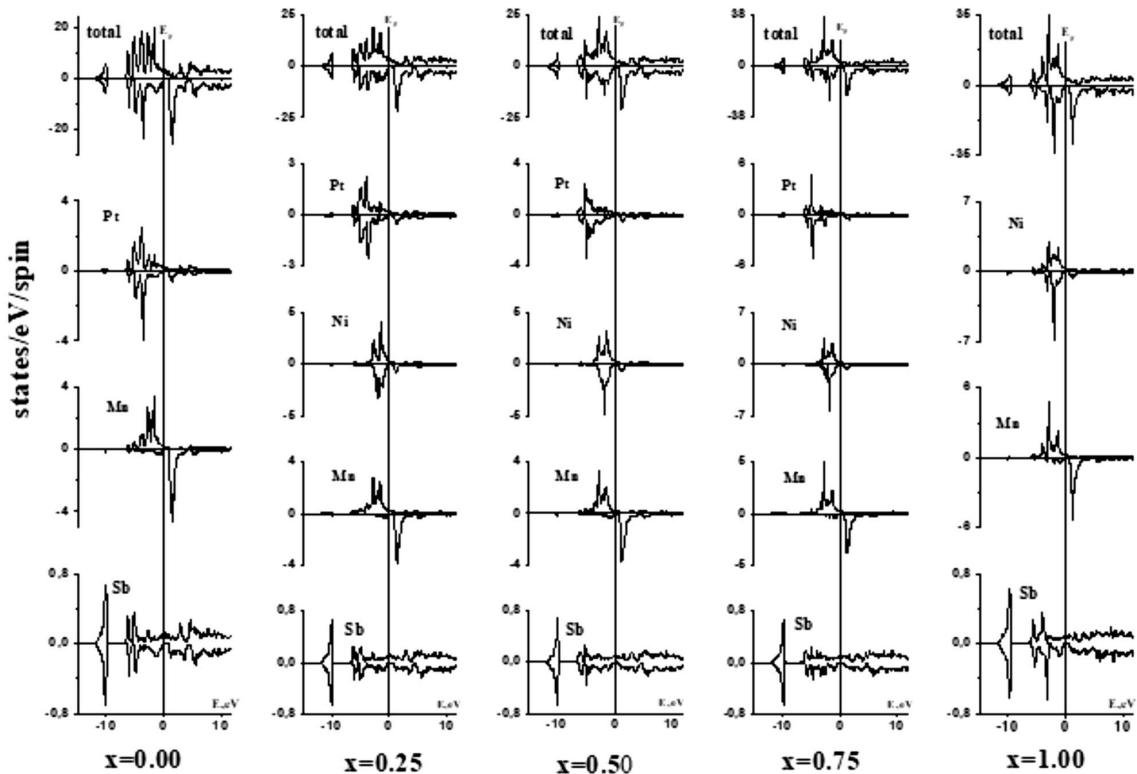
Fig. 3. Total electron densities (top panel) and total atomic electron densities of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$). Densities with positive and negative values correspond to the spin-up and spin-down orientations of the electrons, respectively. E_F is the position of the Fermi level

by considering the energy structure of their valence bands and zones of vacant states. The corresponding data in the form of curves representing the electron state densities are shown in Fig. 3. Total densities and the total atomic densities of the electronic states of the studied phases for both spin orientations are complex structures that change with the atomic composition of the alloys. These changes affect the shape and energy localization of atomic valence states.

The maximum contributions to the densities of states from antimony atoms in all alloys are concentrated in the region of deep-lying ($\sim$$-10$ eV) quasicore states genetically associated with Sb5s- electrons. In general, these contributions are insignificant. The states of antimony atoms in the region of valence electron localization ($0 \div -5$ eV) have even smaller contributions. This indicates that the antimony atoms in the crystal lattices of the alloys are mainly held by ionic bonds.

The localization of the electronic states of metal atoms in this energy region and their hybridization (mixing) indicate that the metal atoms in the alloys are bound together mainly by the covalent interaction. Their further analysis is based on the basic principles of quantum chemistry [21]: in the absence of spatial symmetry constraints, the degree of interactions of the electrons entering into chemical bonds depends on the proximity of their energies and manifests itself in the energy splitting of the final states and the degree of their hybridization.

As can be seen from Fig. 3, the hybridization of the electronic states of metal atoms depends on the atomic composition of the alloys. In the PtMnSb alloy, the states of metal atoms occupy close energy positions, hybridize well, and split energetically. These facts indicate a high degree of covalence of PtMn chemical bonds, which provides high values of the binding energy of PtMnSb alloy (Fig. 1). A consistent increase in nickel concentrations in $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) is accompanied by a decrease in the degree of hybridization of the electronic states of platinum atoms. In the limiting case ($x = 0.75$), the

electronic states of platinum are localized in a narrow energy region remote from those similar for nickel and manganese atoms. The latter remain well hybridized throughout the changes in nickel concentrations, thereby providing covalent Mn–Ni interactions.

Based on these arguments, we can understand the fact that the concentration decrease in the cohesive energies (Fig. 1) of $Pt_{1-x}Ni_xMnSb$ alloys is probably due to a decrease in the covalent interactions of platinum atoms with the surrounding atoms.

It also follows from Fig. 3 that the states of the conductivity bands of the alloys are mainly formed by the electrons of the manganese atoms with a spin-down orientation. Attention is drawn to the discrepancy between the shapes and values of the electron densities corresponding to different spin directions, which indicates the polarization of the electronic states. This effect is most pronounced in manganese.

Polarization effects lead to the appearance of magnetic moments on the atoms. It is useful to consider the question to what extent certain electronic states are involved in the formation of magnetic moments on the atoms of the alloys under discussion? The relevant data are shown in Fig. 4. It can be seen that the determining contributions to the formation of magnetic moments in alloys are assigned to the 3d electrons of manganese atoms. The contributions of Mns, p-electrons are negligible. This can be fully attributed to the electrons of all the symmetries of other metal atoms and antimony in all types of alloys.

Figure 5 shows the concentration dependences of the magnetic moments falling on the formula units of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$). In the experimental work [10], it was noted that the values of these magnetic moments essentially remain constant over the entire interval of nickel concentrations in the alloys. In Fig. 5, this is indicated by a horizontal line, which, according to the authors, is the result of averaging experimental data. These data at the qualitative level coincide with those obtained in this work. Indeed, the calculated values of the magnetic moments practically do not depend on the concentration of nickel atoms in the studied alloys. We recall that the "outliers" of the values of experimentally measured magnetic moments at the content of nickel atoms $x = 0.25$ in alloys are associated [10] with the presence of other phases with concentrations reaching 15%. In general, the samples studied here also contained other phases in concentrations up to
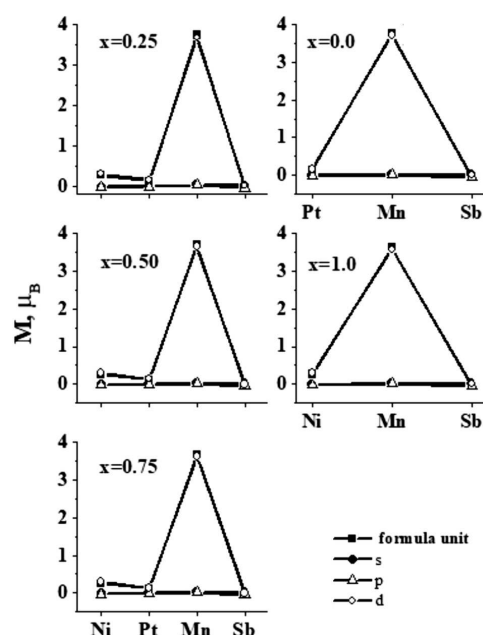

Fig. 4. Partial contribution of electronic states to the formation of magnetic moments (M, μ_B – Boron magneton) on atoms in $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$)

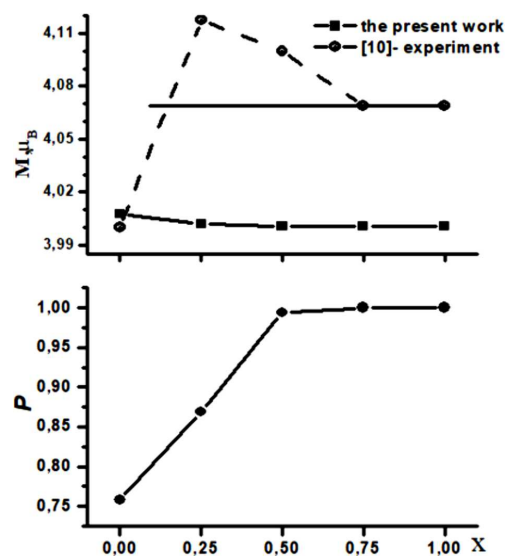**Fig. 5.** Magnetic moments (M) per formula unit of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$). The horizontal solid line in the experimental part of the figure is the result of averaging the measurements [10]. P-electron polarization at the Fermi level in $Pt_{1-x}Ni_xMnSb$ alloys

5%. Perhaps, these reasons led to systematic differences between the experimental and calculated values of magnetic moments. Note that these differences

for most alloys ($x \geq 0.25$) were ~1.5%. As for the initial composition of PtMnSb, the experimental and calculated values of the magnetic moments actually coincided.

Substituting nickel atoms change the polarization P of electrons at the Fermi level (Fig. 5). The transition from the PtMnSb metal alloy with a relatively high ($P = 0.76$) electron polarization to alloys with $x \geq 0.5$ is accompanied by the full polarization of Fermi electrons ($P = 1.0$) and converts these alloys to a half-metallic state.

4. Conclusions

1. With an increase in the concentration of nickel atoms in $Pt_{1-x}Ni_xMnSb$ alloys, the interatomic spatial density of electrons decreases, which leads to a weakening of interatomic covalent bonds and, as a result, to a decrease in the cohesive energies of the alloys.

2. The course of the concentration dependences of the parameters $a(x)$ of cubic crystal lattices of $Pt_{1-x}M_xMnSb$ solid solutions (M = Ni, Cu, Au; $x = 0.0 \div 1.0$) is determined by the ratio of the radii of the substitution atoms and platinum. If this ratio is less than one (M = Ni, Cu), then the dependence a ($x \to 1.0$) has a descending and, in the opposite case (M = Au), an increasing character.

3. The densities of the electronic states of $Pt_{1-x}Ni_xMnSb$ alloys ($x = 0.0 \div 1.0$) are complex structures that vary in shape, energy position, and localization. The zones of valence electrons ($0 \div -5$ eV) of alloys are dominated by hybridized states of metals, while the vacant states are formed mainly by Mn-electrons with spins oriented downwards.

4. Antimony atoms in the crystal lattices of $Pt_{1-x}Ni_xMnSb$ alloys are mainly held by ionic bonds, whereas metal atoms are mainly covalently bound to each other. Covalent interactions are maximal in PtMnSb, and with an increase in nickel concentrations in alloys, they weaken due to a decrease in the role of platinum valence electrons in the formation of chemical bonds.

5. The densities of electronic states with different spin orientations do not correspond to each other, which indicates the polarization of electrons in alloys. Polarization effects lead to the appearance of magnetic moments on the atoms. The determining contributions to the formation of magnetic moments

in alloys are associated with the 3d-electrons of manganese atoms. The values of the magnetic moments practically do not depend on the concentration of nickel atoms in the studied alloys.

6. Substituting nickel atoms change the polarization P of electrons at the Fermi level. The transition from the PtMnSb metal alloy with a relatively high ($P = 0.76$) electron polarization to alloys with $x \geq 0.5$ is accompanied by the full polarization ($P = 1.0$) of Fermi electrons and converts these alloys to half-metallic ones.

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ВПЛИВ АТОМНИХ ЗАМІЩЕНЬ
НА ЕЛЕКТРОННУ СТРУКТУРУ СПЛАВІВ
$Pt_{1-x}Ni_xMnSb$ ($x = 0{,}0$–$1{,}0$)

За допомогою зонних розрахунків у моделі FLAPW (the full-potential linearized augmented-plane-waves) отримано інформацію про енергетичні, зарядові та спінові характеристики сплавів $Pt_{1-x}Ni_xMnSb$ ($x = 0{,}0$–$1{,}0$). Встановлено, що зі збільшенням концентрації атомів нікелю в сплавах $Pt_{1-x}Ni_xMnSb$ зменшується міжатомна просторова густина електронів, послаблюються ковалентні зв'язки і знижуються когезійні енергії сплавів. Домінуючий внесок у формування магнітних моментів у сплавах $Pt_{1-x}Ni_xMnSb$ роблять 3d-електрони атомів марганцю. У сплавах з $x \geq 0{,}50$ зареєстрована повна поляризація фермієвських електронів, що переводить ці сплави в half-metallic стан.

К л ю ч о в і с л о в а: зонні розрахунки, сплави Гойслера, електронна будова, магнітні моменти, поляризовані електронні стани, спінтроніка.