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ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF HEUSLER ALLOYS MMnSb ($M = \mathrm{Ni, Pd, Pt}$)

The energy, charge, and spin characteristics of the MMnSb ($M = \mathrm{Ni, Pd, Pt}$) *alloys have been obtained using band calculations in the framework of the full-potential linearized augmented plane-wave (FLAPW) model. The obtained data show that, owing to an increase of the covalent atomic interaction, the cohesive energies monotonically increase along the alloy series PdMnSb–NiMnSb–PtMnSb, with the indicated alloys being ferromagnetically ordered and characterized by the enhanced localization of magnetic moments at the manganese atoms. It is found that the main contribution to the formation of magnetic moments in the alloys is made by* 3*d-electrons of the manganese atoms. The dominant role is played by electrons on the* t_{2g}*-orbital, and the less one by electrons on the* e_g*-orbital. The contribution of the s- and p-electrons of Mn atoms and the electrons of other atoms to the formation of magnetic moments of the examined alloys is found to be small.*

Keywords: band calculations, cohesive energy, magnetic moments, spintronics.

1. Introduction

The XYZ intermetallics with X and Y cations and Z anions in their crystal lattices generate a wide series of the so-called Heusler alloys (phases). Electropositive elements, which are most often represented by transition metals or rare earths, are studied in this work, whereas electronegative elements belong to metalloids or metals in the other half of the periodic table (these are Si, Sn, Sb, Al, Pb, Bi, and others). The mentioned phases have a characteristic set of magnetic, kinetic, optical, magneto-optical, superconducting, and other important properties. For the group of discussed compounds, topological insulators were managed to realize, as well as the so-called half-metallic state of the solid with the absolutely uncompensated spin density of electrons at the Fermi level, which possesses an important property that is necessary for creating materials for spintronics [1].

Among the first studied Heusler compounds, there were phases with the $L2_1$-structure and the atomic composition X_2YZ. They consist of four fcc sublattices that penetrate one another [2]. Later, there were discovered phases with vacancies in one of those sublattices, the so-called $C1_b$-structures [3]. They are XYZ alloys, and they were called half-Heusler alloys. Accordingly, the former phases were classified as full-Heusler alloys.

Owing to the wide application possibilities of such phases in science and modern technology, a large body of the literature is devoted to the research of their various properties. The story of corresponding studies, as well as their scope and details, can be learned through the reading, e.g., of excellent works [1, 4, 5]. In those works, as well as in other relevant publications, the structural, optical, magnetic, magneto-optical, kinetic, and a number of other properties of Heusler phases were most often considered. Moreover, the cited publications and the discussion of their results mainly concern only one of the mentioned types of Heusler phases, for example, half-Heusler compounds [6–11].

There is a series of works dealing with band calculations for the compounds mentioned above [3, 12–15]. In those works, the energy band structure of the alloys and the magnetic moments of atoms and crystal unit cells were considered, evidence of that some compound belongs to a half-metallic series was given, and the influence of the atomic substitution and the formation of an atomic disorder on the electronic structure parameters of researched compounds was analyzed. As a shortcoming of the indicated works, we may indicate an insufficient elucidation of the influence exerted by the atomic structure of the compounds on their electronic structure.

From the viewpoint of band calculations, a convenient model system is a series of half-Heusler alloys with the general formula MMnSb, where $M =$ Ni, Pd, and Pt are elements belonging to the same group in the periodic table with ten valence d- and s-electrons, and the monotonically increasing principal quantum number n. In addition, all those alloys mainly crystallize in the cubic syngony with the spatial symmetry group F-43m (Fedorov group No. 216), which thus eliminates the issue about the influence of changes in the spatial structure on the electronic structure of those compounds. An interesting fact about those alloys is that the works cited above contain no comparative data on the binding energies of their atoms (the cohesive energies), the structures of electronic states, the changes in the atomic spin states that determine their magnetic moments and the magnetic moment of the whole lattice, and the contributions of partial electronic states to those moments. This work is devoted to the search for answers to the posed questions.

2. Research Methods

In this work, band calculations of the electronic structure for the Heusler alloys MMnSb ($M =$ Ni, Pd, Pt) were carried out using their structural data taken from works [9, 11, 16]. The data were determined at room temperatures. According to the obtained information, the distribution of non-equivalent atoms over the Weisskopf positions in the lattices of the examined alloys is as follows: the atoms M occupy the position 4$\boldsymbol{c}$ (0.25, 0.25, 0.25), whereas the manganese and antimony atoms do the positions 4$\boldsymbol{b}$ (0.5, 0.5 , 0.5) and 4$\boldsymbol{a}$ (0.0, 0.0, 0.0), respectively. Here, the atomic coordinates (x, y, z) are indicated as the fractions of the unit cell edges in the alloys. The values of the cubic cell parameter $\boldsymbol{a}$ that were used in the calculations for the alloys with nickel, palladium, and platinum were equal to 5.929, 6.285, and 6.201 Å, respectively. The calculations were carried out in the framework of the density functional theory (DFT), using the full-potential linearized augmented plane-wave (FLAPW) model [17], and with the gradient approximation for the electron density (the GGA-generalized gradient approximation) taken from work [18]. While calculating the characteristics of the electronic structure, the spin-polarized version of the FLAPW method was applied [19].

The radii of the muffin-tin (MT) atomic spheres, R_{MT}, were chosen to minimize the size of intersphere region II in the NiMnSb alloy, which is characterized by the smallest unit cell volume. For all phases and all atoms in them, those radii amounted to 2.18 a.u. (1 a.u.$= 5.2918 \times 10^{-11}$ m). When calculating the parameters of the phase electronic structure in the discussed compounds, 165 points in the irreducible part of the Brillouin zone were used. The APW+lo bases were used to approximate the wave functions of d-electrons in all atoms, and the LAPW bases to approximate the wave functions of other valence electrons [19]. The size of the basis set was determined by the product $R_{\mathrm{MT}}K_{\max} = 7.0$, where $K_{\max}$ is the maximum magnitude of the reciprocal lattice vector. The value $l = 10$ was selected for the maximum orbital quantum number of the partial waves within the MT spheres, and the value $l = 4$ when calculating the non-muffin-tin matrix elements.

The binding energy values were calculated as the difference between the total energies of the atoms that form a unit cells in the alloys and the sum of the total energies of their constituent atoms “infinitely” separated from one another, which were determined following the recommendations of work [20].

When calculating the average value of the spatial electron density q in interspherical region II, the volume of the latter in cubic angströms and the total electron charge localized in this volume were used.

3. Discussion of Results

When studying a group of compounds, one of the most important comparative characteristics is the binding energy of their atoms. Those energies were calculated in this work for the researched alloys and

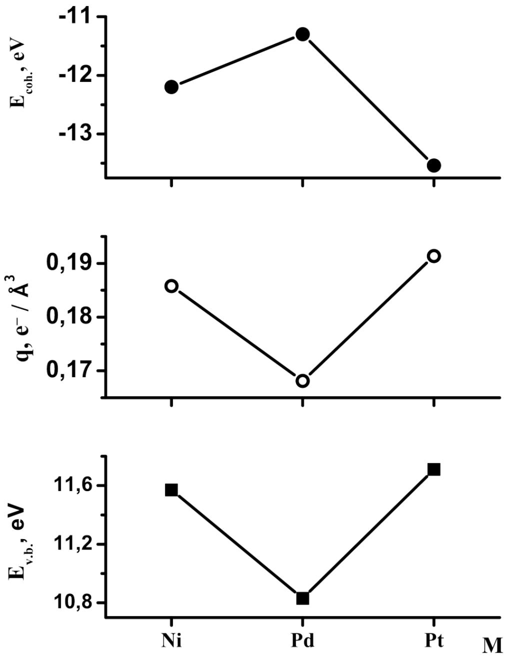

Fig. 1. Binding energies (E_{coh}) of atoms (upper panel), the averaged electron charge density q in the interatomic space (e^- is the electron charge, middle panel), and the valence band width ($E_{\mathrm{v.b.}}$, lower panel) in the MMnSb alloys (M = Ni, Pd, Pt)

are graphically presented in Fig. 1. Figure 1 also illustrates the data on the averaged spatial densities of electrons located in their interatomic region, q, and the quantitative changes of the valence bandwidth, $E_{\mathrm{v.b.}}$. It is quite clear [21] that the growth of the q- and $E_{\mathrm{v.b.}}$-values testifies to an increase of the covalent character of interatomic bonds. For this reason, the symbatic behavior of both curves reflecting the dependence of the indicated quantities on the atomic composition of alloys also becomes clear. From the presented data, it follows that the both characteristics change in the opposite ways with respect to the atomic binding energies, E_{coh}, in the MMnSb alloys (M = Ni, Pd, Pt). The largest atomic binding energy corresponds to the alloy with platinum, and the lowest value of E_{coh} is inherent to the compound with palladium, with the phase with nickel being charged by an intermediate value of this parameter. This dependence correlates with the covalence degree of interatomic bonds corresponding to the q- and $E_{\mathrm{v.b.}}$-values. Namely, this degree is maximum for the platinum phase, minimum for the alloy with palladium, and intermediate for the alloy with nickel.

Additional information about the nature of chemical bonds in the studied alloys can be obtained by considering the energy structure of their valence bands and vacancy zones. The corresponding data are shown in Fig. 2 in the form of curves reflecting the density of electronic states. The total density of electronic states for both spin orientations in the studied alloys is a complicated structure that substantially changes with the variation of their atomic composition. The spin states oriented downward are characterized by a low density at the Fermi level, diminishing to zero for the nickel phase. Those facts testify that the nickel alloy is a typical half-metallic semimetal, whereas the other compounds are typical metals with a high polarization degree of electronic states at the Fermi level. Those facts are also consistent with the results obtained earlier in the framework of band approaches to the structure of the electronic state density near the Fermi level [22].

Currently, there are no experimental data in the literature that would confirm the conclusion about the densities of electron states with oppositely directed spins at the Fermi level in the discussed alloys. Recall that resistive measurements of the alloys with nickel and platinum point to close values of 7×10^{-8} and 6.8×10^{-8} Ω m, respectively [6], which are characteristic of iron and tungsten. From Fig. 2, it follows that the total electron density of states in the alloys is a result of the hybridization of the total atomic electronic states with a substantial participation of the states of the metal atoms. The contributions made by the antimony atoms turned out to be inconsiderable and mainly responsible for the formation of deeply located (at about $-5 \div -10$ eV) quasicore states that are genetically related to the 5s-electrons of Sb. The low electron density given by the antimony atoms just in the valence state interval ($0 \div -5$ eV) may testify that the valence bond in the lattices of the examined alloys is mainly realized through ionic bonds. The localization of the electronic states of metal atoms dominates in this energy interval, and the high degree of their hybridization testifies that the metal atoms in the researched alloys are mainly connected with one another via covalent interactions.

Attention is attracted by the discrepancy between the shapes and the values of the electron density corresponding to different spin directions. This fact testifies to the polarization of the electronic states, which mainly manifests itself in the states of man-

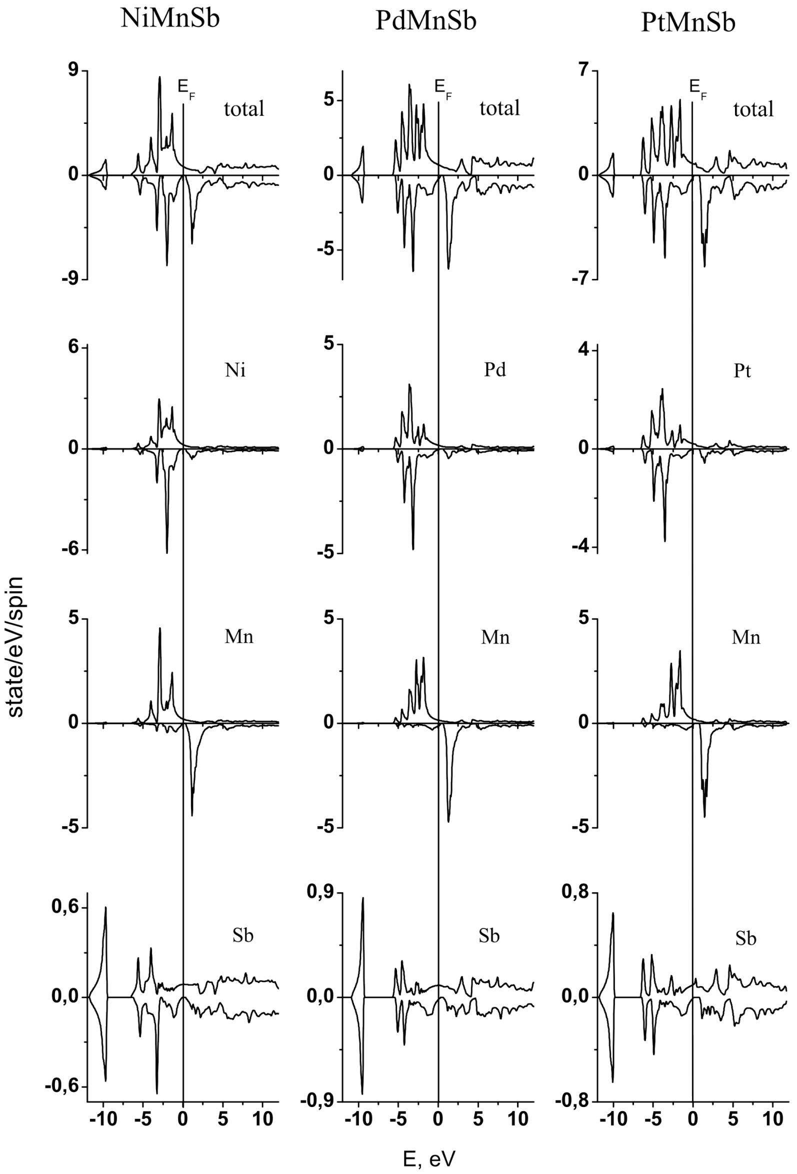

Fig. 2. Total densities of electron states and total atomic densities of electron states in the MMnSb alloys (M = Ni, Pd, Pt)

ganese atoms and, in whole, in the total electronic states of the alloys. The mentioned polarizations result in the appearance of magnetic moments in the alloys, the magnitudes of which were calculated in this work (they are quoted in Table). The antimony atoms are characterized by the smallest magnitudes of the magnetic moment, with the latter being negative. The magnetic moments of other structural fragments are positive, which testifies to the existence of conditions favorable for an ordering of the ferromagnetic type to occur in the studied alloys.

Magnetic and neutron-diffraction measurements for the nickel-containing alloy actually point to the ferromagnetic type of ordering with the critical temperature of the transition into the paramagnetic state T_c = 760 K [8]. This conclusion is confirmed by the results of work [23], where the close value T_c = 750 K was registered for the critical temperature. From the

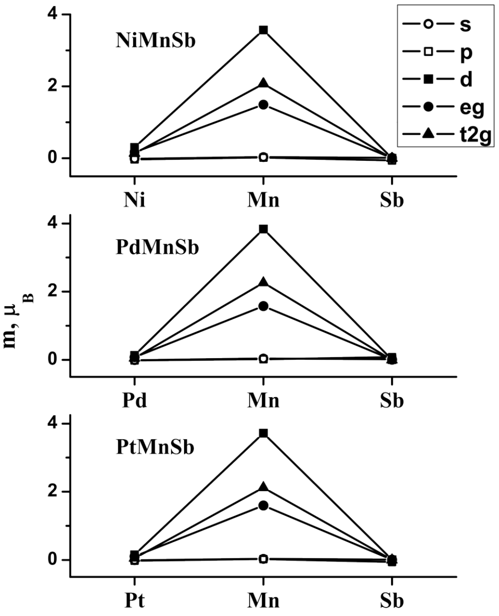

Fig. 3. Partial contributions of electronic states to the formation of atomic magnetic moments m in the MMnSb alloys (M = Ni, Pd, Pt)

data quoted in Table, it follows that the largest magnetic moments are localized at the manganese atoms of the alloys, whereas the magnetic moments of metal atoms and in the interspherical region are relatively small. A good experimental confirmation of this conclusion is, in particular, the data on the magnetic moments of the manganese atoms obtained in the already cited works [8, 23]: 4.0 and 3.85 times the Bohr magneton. μ_B, respectively.

Experiments showed as well that the palladium-containing alloy is also characterized by ferromagnetism with the critical phase transition temperature $T_c = 500$ K [6], with a magnetic moment of $3.95\mu_\mathrm{B}$, being localized at the manganese atoms [24].

Neutron-diffraction and magnetometry data [7, 8] qualitatively confirm the results obtained in this work: the alloy with platinum is a ferromagnet with $T_c = 572$ K and the localization of the largest magnetic moment at the manganese atoms. There is a quantitative mismatch of the magnetic moment values quoted in Table with a value of $4.02\mu_\mathrm{B}$ obtained experimentally [8].

Magnetic moments (in Bohr magneton units, μ_B) at the atoms, in the unit cell, and in the region outside the MT spheres (region II) in the MMnSb alloys (M = Ni, Pd, Pt)

Alloy	M	Mn	Sb	Cell	II
NiMnSb	0.267	3.623	−0.044	4.001	0.155
PdMnSb	0.108	3.894	−0.061	4.105	0.163
PtMnSb	0.127	3.769	−0.046	4.009	0.158

The authors of the experimental works cited above noted that the effective magnetic moment of the unit cells in the considered alloys is close to $4.0\mu_\mathrm{B}$. The same value was obtained in this work as well, which testifies to a good quality of our calculations.

It is useful to consider the issue concerning the extent to which various electronic states are engaged in the formation of magnetic moments at the atoms in the researched alloys. The corresponding data are illustrated in Fig. 3. One can see that the main contribution to the formation of magnetic moments in the alloys is made by the 3d-electrons of the manganese atoms. More specifically, the dominant role is played by the electrons of the t_{2g}-orbital and, to a less extent, by the electrons of the e_g-orbital. The contributions of the s- and p-electrons of Mn turn out very small. The same is valid for the electrons of all symmetries in the atoms of other metals and antimony in the alloys of all types.

4. Conclusions

1. In the sequence of alloys PdMnSb → NiMnSb → → PtMnSb, the values of the binding energy (cohesive energy) of atoms increase owing to the growth of the covalence degree of atomic interaction. The antimony atoms in the lattices of the indicated alloys are mainly held by ionic bonds, whereas the metal atoms are bound with one another mainly via covalent interactions.

2. In the alloy series MMnSb (M = Ni, Pd, Pt), the nickel-containing phase is a typical half-metallic semi-metal, whereas the alloys with palladium and platinum are ordinary metals with the high degrees of electronic state polarization at the Fermi level.

3. The MMnSb alloys (M = Ni, Pd, Pt) are ferromagnetically ordered with an enhanced level of the magnetic moment localization at the manganese atoms. The main contribution to the formation of magnetic moments of the alloys is made by 3d-electrons of the manganese atoms, with the dominant role being played by the electrons of the t_{2g}-orbital and, to a less extent, by the electrons of the

e_g-orbital. At the same time, the contributions of the s- and p-electrons of the Mn atoms to the formation of the magnetic moments of the researched alloys are small.

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ЕЛЕКТРОННА БУДОВА ТА МАГНІТНІ ВЛАСТИВОСТІ СПЛАВІВ ГЕЙСЛЕРА: MMnSb ($M = \mathrm{Ni, Pd, Pt}$)

Методами зонних розрахунків у моделі FLAPW (the full-potential linearized augmented-plane-wave) отримано інформацію про енергетичні, зарядові та спінові характеристики сплавів MMnSb ($M = \mathrm{Ni, Pd, Pt}$). Отримані дані свідчать про те, що за рахунок росту ковалентної взаємодії атомів когезійні енергії зростають у послідовності сплавів PdMnSb → NiMnSb → PtMnSb, а самі сплави феромагнітно впорядковані, з підвищеною локалізацією магнітних моментів на атомах марганцю. Отримано, що основний внесок у формування магнітних моментів сплавів дають $3d$-електрони атомів марганцю. При цьому домінуюча роль його електронів припадає на t_{2g}- і в меншій мірі e_g-орбіталі. Внески ж s,p-електронів марганцю і електронів інших атомів у формування магнітних моментів сплавів виявляються малими.

Ключові слова: зонні розрахунки, когезійна енергія, магнітні моменти, спінтроніка.