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2000 J. Phys.: Condens. Matter 12 8127

(http://iopscience.iop.org/0953-8984/12/37/311)

J. Phys.: Condens. Matter **12** (2000) 8127–8134. Printed in the UK PII: S0953-8984(00)12885-1

Effect of vacancies on the electronic structure of Pd_xTiSn alloys

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Received 28 March 2000, in final form 30 May 2000

Abstract. We have studied the influence of vacancies on the electronic structure of Pd_xTiSn ($1 \leqslant x \leqslant 2$) Heusler-type alloys by the *ab initio* tight binding linearized muffin-tin orbital (TB LMTO) method. The LMTO calculations have shown that PdTiSn can be classified as a narrow gap semiconductor with the gap equal to 0.4 eV. The gap vanishes for $x > 1.125$. The calculations have shown that the local chemical disorder in PdTiSn depresses the gap. The lattice parameter obtained from the minimum of the total energy is constant for $1.5 \leqslant x \leqslant 2$ and for $x < 1.5$ its value decreases.

1. Introduction

In a group of cubic semi-Heusler type alloys which crystallize in a cubic structure of the MgAgAs type an indirect gap was observed [1–7]. The series of the intermetallic semi-Heusler alloys (CoTiSn, CoTiSb, NiTiSn, NiTiSb) was investigated experimentally and theoretically by Toboła and co-workers [5]. They observed in these systems the transition from semiconductor to metal, from Pauli-like to a Curie–Weiss paramagnet and from the paramagnetic to ferromagnetic ground states. Ogut and Rabe [6] used the pseudopotential total-energy method to investigate the stability and electronic structure of the ternary intermetallic semi-Heusler NiMSn (M = Ti, Zr, Hf). They found in these systems an indirect semiconducting gap near 0.5 eV. Ślebarski and co-workers [9] studied the effect of substitution of Zr and Ti by Ce on the electronic structure of NiZrSn and NiTiSn semi-Heusler alloys. These alloys are classified as narrow gap semiconductors with an indirect gap near 0.5 eV. The gap in NiZrSn was strongly dependent on the vacancy site and was not observed for vacancies located at Sn or Zr sites [9]. The gap was also suppressed by a partial substitution of tetravalent ions (Zr or Ti) by trivalent Ce. Ślebarski *et al* [9] suggested that the gap was formed for a tetravalent element which strongly hybridized with the conduction band states. The value of the indirect gap is also suppresses by the local chemical disorder in sublattice. The experimental measurements indicated that the value of the gap in semi-Heusler alloys changed from $\Delta = 0.1$–0.5 eV [1–9]. The influence of vacancies on electronic and magnetic properties of $Ni_{2-x}TiSn$, $Co_{2-x}TiSn$, $Co_{2-x}ZrSn$ alloys was studied recently both experimentally and theoretically [1–8]. In $Ni_{2-x}TiSn$ and $Ni_{2-x}ZrSn$ the transition from metal to semiconductor was observed [1, 7]. The dilution of $Co_{2-x}ZrSn$ leads to the change of the crystallographic structure from cubic ($L2_1$) to hexagonal (Fe_2P) [8] and CoZrSn is a Pauli paramagnet with a low density of states at the Fermi level [8]. The electronic and magnetic properties of series $Pd_{2-x}Co_xTiSn$ and $Pd_{2-x}Ni_xTiSn$ Heusler type alloys have been studied in recent years [10–14]. Jezierski [13, 14] calculated the electronic structure and magnetic properties of $Pd_{2-x}Co_xTiSn$ alloys for the different distribution of Pd and Co

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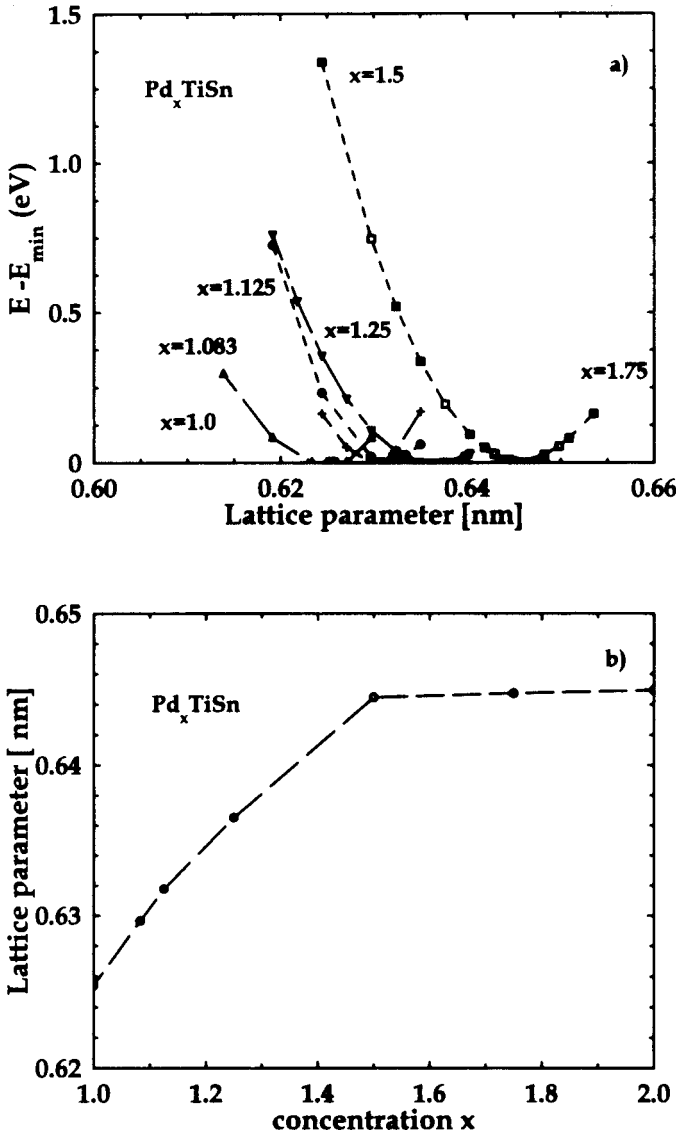


Figure 1. (a) The dependence of the total energy on the lattice parameters. (b) The plot of theoretical lattice parameters against concentration obtained from the minimum of the total energy.

atoms onto sublattices. The calculated total magnetic moment increased with the increase of Co concentration. The spin-polarized TB LMTO calculations indicated the magnetic phase transition from the paramagnetic to ferromagnetic states for $x > 0.5$ [13].

In this paper we present the influence of dilution on the electronic structure of Pd_xTiSn alloy for $1 \leqslant x \leqslant 2$. Using the *ab initio* LMTO method we try to give answer whether the cubic semi-Heusler PdTiSn alloy is a semiconductor or metal. The band structure of Pd_2TiSn was investigated by ultraviolet photoemission spectroscopy (UPS) [15, 16] and x-ray photoemission spectroscopy (XPS) [10, 17]. The UPS measurements [15, 16] have shown that the valence band extends to 7–8 eV below the Fermi level. The main contribution to the

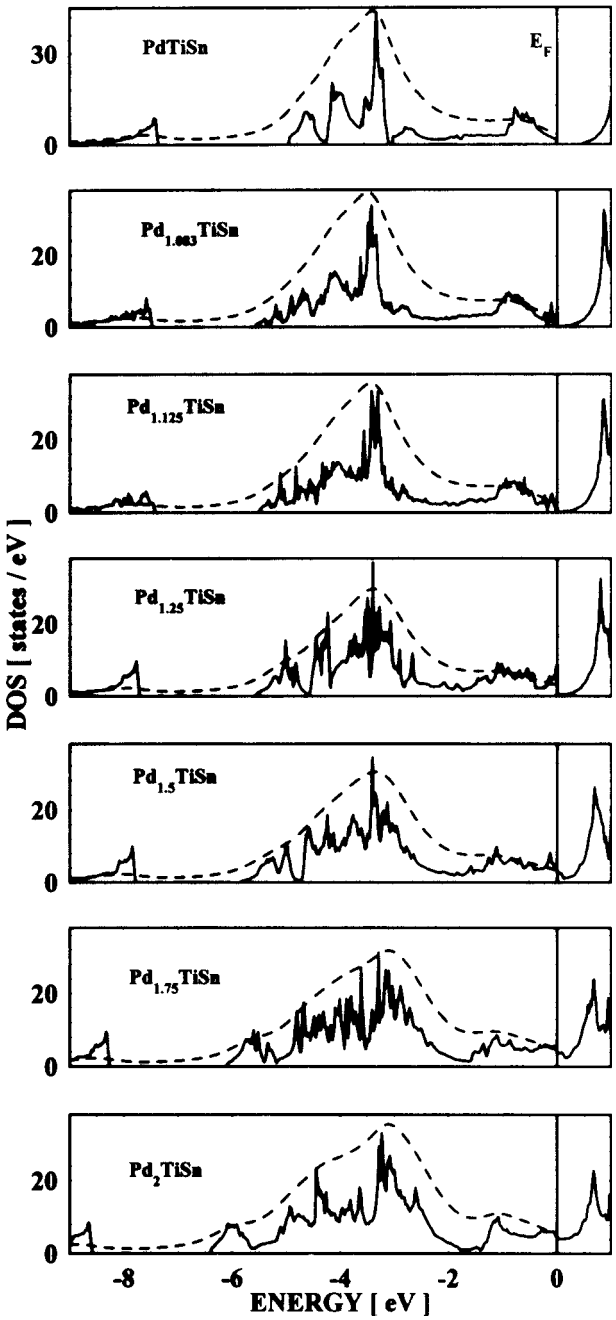


Figure 2. The electronic density of states for Pd_xTiSn. The dashed curves show the DOS convoluted by Lorentzians of half-width 0.4 eV and multiplied by photoelectric cross-sections [23].

density of states at the Fermi energy comes from Ti 3d states and Pd 4d states. The shape of the density of states for Pd_2TiSn was also confirmed by XPS [10]. The theoretical *ab initio* LMTO calculations for Pd_2TiSn [12–14] were in good agreement with UPS and XPS measurements.

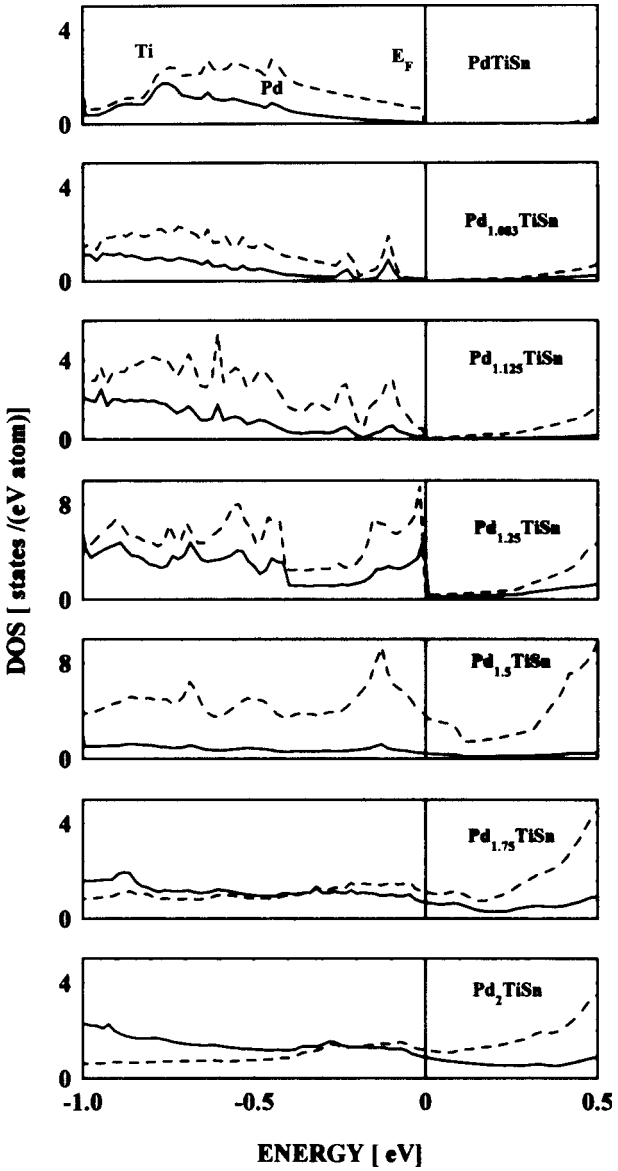


Figure 3. The partial DOS for Pd (solid line) and Ti (dashed line) near the Fermi energy.

In this work the band structure of Pd_xTiSn was calculated by the TB LMTO method [18–20] for the lattice parameters determined from the minimum of the total energy. We pay attention to the change of the band structure near $x = 1$ i.e. in the region when the transition from metal to semiconductor is observed.

2. Method of calculation

The electronic structure was calculated by the *ab initio* self-consistent tight binding linear muffin tin orbital (TB LMTO) method [18–20] within the atomic sphere approximation (ASA).

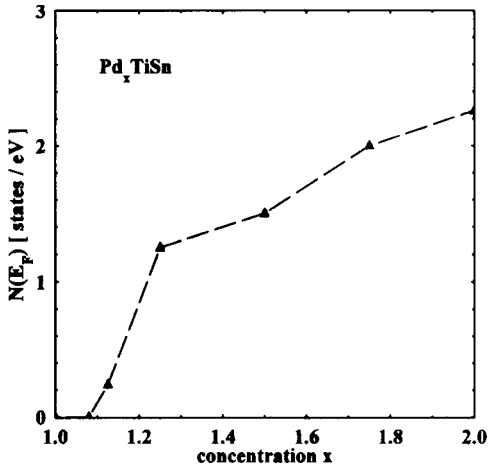


Figure 4. The dependence of the density of states at the Fermi energy $N(E_F)$ in Pd_xTiSn.

The scalar-relativistic approximation for band electrons and the fully relativistic treatment of the frozen core electrons were applied. The values of the atomic sphere radii were taken in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. The exchange correlation potential was taken in form proposed by von Barth and Hedin [21, 22]. The self-consistent spin-polarized band calculations were performed for 270 k points in the irreducible wedge of the Brillouin zone. The cubic $L2_1$ structure of Pd_2TiSn consists of four interpenetrating fcc sublattices: two with the origins at (000) (Ti), (0.5 0.5 0.5) (Sn), and two sublattices taken by the Pd atom located at (0.25 0.25 0.25) and (0.75 0.75 0.75). In the band calculations we replaced each fcc sublattice by four simple cubic (sc) sublattices. In this way our unit cell contains 16 atoms. The dilution of Pd_2TiSn to PdTiSn is connected with decrease of Pd atoms on one palladium sublattice. Such geometrical model gives the possibility to change the concentration of Pd with step of 0.25. In order to study exactly the transition from metal to semiconductor near PdTiSn ($x = 1$) we have performed the additional band calculation for 32 and 48 atoms unit cell, which gives the possibility to change the Pd concentration with step of 0.125 and 0.083.

3. Results and discussion

For each concentration x ($x = 2.0$, 1.75, 1.5, 1.25, 1.125, 1.083, 1.0) we have performed the self-consistent band calculations. The values of the lattice parameters were determined from the minimum of the total energy, because such system was not studied experimentally up to now. In figure 1(a) we present the dependence of the total energy (the difference between energy calculated for the given lattice parameter and the energy corresponding to the minimum) on the lattice parameters. The dependence of the theoretical lattice parameter (obtained from the minimum of the total energy) on the concentration x is plotted in figure 1(b). Our theoretical results indicate that up to $x = 1.5$ the lattice parameter is constant and has the same value as for Pd_2TiSn. For $x < 1.5$ the values of lattice parameters decrease to $a = 0.625$ nm.

In the band calculations we assume that one fcc sublattice is occupied by palladium atoms and we change the number of Pd only in the second fcc (four simple cubic) sublattice. For $x = 1.125$ and $x = 1.083$ we used a unit cell that consists of 32 and 48 atoms, respectively. The spin-polarized band calculations have shown that all systems are paramagnetic. The local

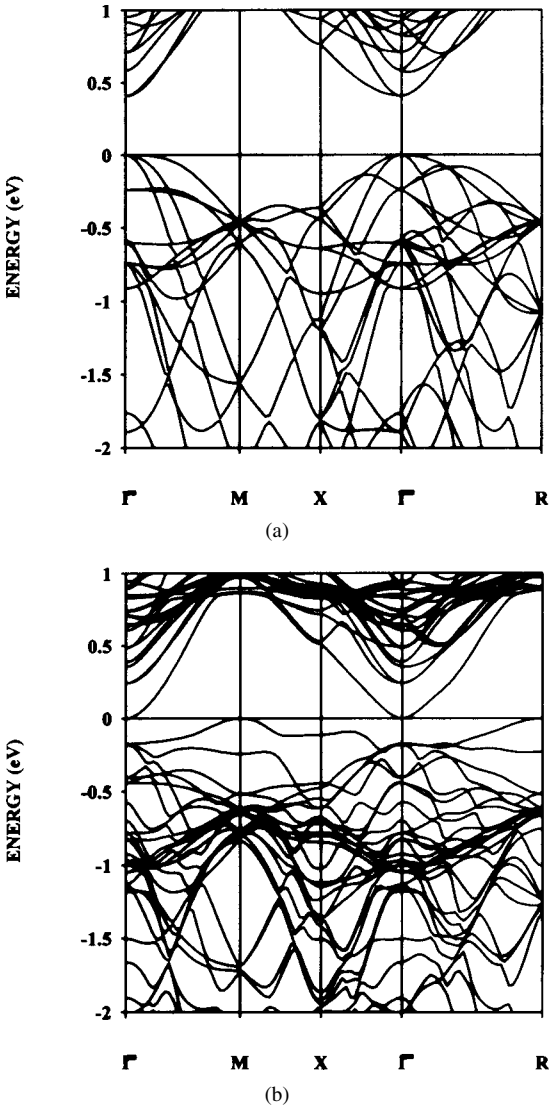
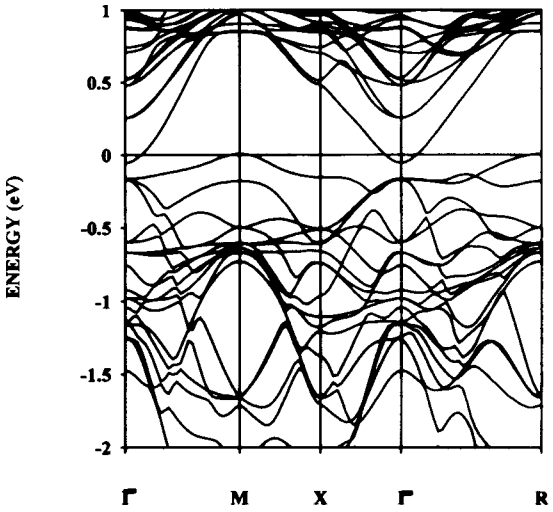


Figure 5. Dispersion curves along high-symmetry directions in the Brillouin zone of paramagnetic Pd_xTiSn. (a) $x = 1.0$, (b) $x = 1.083$, (c) $x = 1.125$.

chemical disorder (the vacancies distributed on two palladium sublattices) do not give any magnetic moments. The effect of local disorder in PdTiSn will be discussed later.

The total density of states (DOS) for paramagnetic Pd_xTiSn is presented in figure 2. The electronic structure of Pd_2TiSn was discussed in detail in the previous papers [12–14] and we treat it as the reference system. The UPS measurements [15, 16] showed that the density of states at the Fermi level consists of two contributions from Pd 4d and Ti 3d states. In the total DOS for Pd_xTiSn below the Fermi level we observe three peaks. The lower small peak near $E = -8$ eV corresponds to Sn 3s states. The broad peak in the range $-7 < E < -2$ eV gives the contribution mainly from palladium 4d states. The small peak below the Fermi level is connected to Pd 4d and Ti 3d states.



(c)

Figure 5. (Continued)

In figure 2 the dashed lines show the theoretical photoemission spectra (the density of states convoluted by Lorentzians of half-width 0.4 eV and taking into account appropriate cross sections for the partial bands [23]). In the spectra we observe one peak located in the range $-6 < E < -2$ eV. The shape of this peak is modified with the change of palladium concentration. For PdTiSn the width of the peak is less than for Pd_2TiSn. The theoretical photoemission spectra can be verified by the x-ray photoemission (XPS) measurements.

We pay special attention to the region near the Fermi level. In figure 3 we present the contribution to the electronic density of states from Pd (solid line) and Ti (dashed line). For $x = 2$ the contributions from Pd and Ti are similar. In the region $1.25 < x < 1.75$ the value of $N_{Ti}(E_F)$ increases. For $x < 1.125$ the value of $N(E_F)$ goes to zero, i.e. the contributions from Pd and Ti are also zero. For $x = 1.25$ the Fermi level is located on the right-hand side of sharp peak. We increased the number of k points in the irreducible wedge of the Brillouin zone up to 450, but the values of density of states at the Fermi level was almost the same. The dependence of $N(E_F)$ on concentration is plotted in figure 4. The density of states at the Fermi level increases with increase of palladium concentration. The change from metal to semiconductor starts from $x < 1.083$.

The transition from metal to semiconductor can be observed in the plots of the band structure along the symmetry directions in the Brillouin zone. In figure 5 we present the energy bands for $x = 1.0$ (figure 5(a)), $x = 1.083$ (figure 5(b)) and $x = 1.125$ (figure 5(c)) along the high-symmetry lines of the Brillouin zone. The indirect gap is observed in the Γ direction for $x = 1$ and $x = 1.083$. For $x = 1.125$ only a few bands cross the Fermi level and the density of states $N(E_F)$ is small.

We have also studied the effect of local disorder in Pd sublattices. The vacancies were distributed randomly onto Pd sublattices. The local disorder leads to increasing of the total energy. We pay special attention to the PdTiSn alloy. The random distribution of vacancies in the two Pd sublattices reduces the gap and system has metallic character.

4. Conclusions

In this paper we have presented the effect of dilution in Pd_xTiSn alloys. Our *ab initio* LMTO calculations of the electronic structure have shown that PdTiSn can be classified, similar to NiTiSn and NiZrSn, as a semiconductor material with an indirect gap of 0.4 eV. The nature of the gap is connected to the 3d density of states of Ti. The gap is formed as an effect of strong hybridization between 3d Ti and 4d Pd states. The 3d Ti states move towards lower energy with increasing x concentration. The gap is destroyed with increasing Pd concentration and the vacancies at Ti and Sn sites. The d states of Pd and Ti are located close to the Fermi level and there is a strong hybridization effect between Pd and Ti states.

Ab initio TB LMTO band calculations indicate that the effect of local environment in cubic semi-Heusler alloys plays an important role.

Acknowledgments

This research was supported by the State Committee for Scientific Research through the project No 8 T11F 027 16. The calculations were made in the Supercomputing and Networking Centre of Poznań.

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