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# Electronic structure in ternary intermetallic Pd<sub>2</sub>TiX (X = Al, Ga, In) Heusler-type alloys: are they magnetic?

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**Abstract.** The recent measurements of the magnetic properties of Pd<sub>2</sub>TiIn and Pd<sub>2</sub>TiAl Heusler-type alloys motivated a study of the electronic structure of such compounds. The electronic structures of the ordered Pd<sub>2</sub>TiX (X = Al, Ga, In) Heusler-type alloys are calculated by the self-consistent spin-polarized TB LMTO method. The results indicate that these systems are non-ferromagnetic, while antiferromagnetism has not been investigated.

## 1. Introduction

In recent years the electronic and magnetic properties of Heusler-type alloys have been studied both experimentally and theoretically. Recently, Neumann and co-workers [1–3] observed unusual magnetic properties in the new series of ternary intermetallic Pd<sub>2</sub>TiIn and Pd<sub>2</sub>TiAl compounds, the constituent elements of which were not magnetic as elemental solids. The Pd<sub>2</sub>TiX (X = Al, In) alloys crystallize in an L2<sub>1</sub>-type structure. Measurements [1] of the bulk susceptibility have shown that the Pd<sub>2</sub>TiIn compound was antiferromagnetically ordered below 110 K, with a large effective magnetic moment ( $m = 4.9\mu_B$  fu), as in the Pd<sub>2</sub>MnIn system [4]. However, a recent powder neutron diffraction experiment [2] suggested that the ground state was ferrimagnetically ordered, and a first-order structural transition at 92 K from a tetragonal to a cubic structure was observed. During the structural transformation Ouladdiaf and co-workers [2] did not observe a change in volume of the cell nor any long-range magnetic order below 92 K.

Early measurements of the magnetic properties of Pd<sub>2</sub>Mn(In, Sn) Heusler systems [4] had shown that the magnetic properties depended strongly on the electron concentration. Neumann and co-workers [3] observed a small magnetic moment in Pd<sub>2</sub>TiAl ( $m = 0.21\mu_B$  fu) and in Pd<sub>2</sub>TiSn ( $m = 0.005\mu_B$  fu) alloys [3]. Measurements [1–3] suggested that the small magnetic moment was connected with the d band of titanium. Recently Neumann and co-workers [3] have shown that the value of the magnetic moment in the Pd<sub>2</sub>TiAl alloy depends on the heat treatment of the sample. These unusual properties, and the apparent inconsistency of experimental data, motivated us to study the influence of the III B elements of the periodic table (Al, Ga, and In with the valence configuration  $s^2p^1$ ) on the electronic structure of the Pd<sub>2</sub>TiX ordered alloys.

## 2. Method of calculation of the electronic structure

The electronic structures of the ordered Pd<sub>2</sub>TiAl, Pd<sub>2</sub>TiGa and Pd<sub>2</sub>TiIn alloys were calculated by using the spin-polarized self-consistent TB LMTO method [5], within the framework of

the local spin density (LSD) approximation. The von Barth–Hedin form of the exchange correlation potential [6] was used. The atomic sphere approximation (ASA) was employed and the standard combined corrections [5] for overlapping were applied. The self-consistent band calculations were carried out for more than 150  $k$ -points in the irreducible wedge of the Brillouin zone. In the band calculations the following initial configurations were assumed; for Al: core +  $3s^2p^1$ ; for Ga: core +  $4s^2p^1$ ; for In: core +  $5s^2p^1$ ; for Ti: core +  $3d^24s^2$ ; and for Pd: core +  $4d^{10}$ . The electronic structure for the cubic  $\text{Pd}_2\text{TiAl}$  was computed for the experimental lattice parameter [3]; however, in the case of the  $\text{Pd}_2\text{TiGa}$  system the lattice parameter was estimated from the minimum of the total energy. For  $\text{Pd}_2\text{TiIn}$ , calculations were performed for the experimental lattice parameters [1, 2] both for the cubic ( $c/a = 1.0$ ) and tetragonal ( $c/a = 0.986$ ) structures. The values of the Wigner–Seitz radii in the atomic sphere approximation (ASA) were chosen so as to satisfy the condition

$$\sum_n (S_n/S)^3 = N$$

where  $S = a(3/4\pi N)^{1/3}$ . Here  $a$  denotes the lattice parameter,  $N$  is the number of atoms in the cell, and the summation is over atoms in the cell. The following relations between the radii of atoms, as calculated by Andersen and Kumm [7], were assumed:  $S_X/S = 1.13$ ,  $S_{\text{Pd}}/S = 0.89$  and  $S_{\text{Ti}}/S = 1.047$ .

### 3. Results

The total density of states (DOS) for the  $\text{Pd}_2\text{TiAl}$ ,  $\text{Pd}_2\text{TiGa}$  and  $\text{Pd}_2\text{TiIn}$  alloys are presented in figure 1(a)–(c). The positions of the Fermi levels ( $E_F$ ) are marked by the vertical lines. The Fermi level is located near  $-0.1$  Ryd in the small peak in the DOS. The total DOS (figure 1) for  $\text{Pd}_2\text{TiAl}$ ,  $\text{Pd}_2\text{TiGa}$  and  $\text{Pd}_2\text{TiIn}$  consists of the lower part (below  $-0.6$  Ryd), which contains the  $s$  states of the element X, and the middle part (between  $-0.5$  Ryd and  $-0.2$  Ryd), which gives mainly contributions from the  $d$  states of Pd.

The shape of the total DOS does not change drastically with the substitution of the non-magnetic element (Al, Ga and In). However, there are quantitative differences in the width and position of the gap between  $s$  states of X and  $d$  states of Pd. In figure 2 we plot the partial density of states (PDOS) for  $s$ - $p$  Al (a),  $s$ - $p$  Ga (b), and  $s$ - $p$  In (c). The contributions from the  $d$  states of Ti and Pd are presented in figure 3(a) and (b), respectively.

From the analysis of the partial DOS near the Fermi level it follows that the main contributions to the density of states at the Fermi energy  $n(E_F)$  come from the  $d$  states of Pd and Ti atoms. The values of  $n(E_F)$  are in the range 24–25 states per Ryd cell spin depending on the particular element X. The occupation numbers for orbital states of atoms are listed in table 1. Changing X does not significantly modify the numbers of electrons on Pd and Ti. An increase in the number of  $d$  electrons on Pd and Ti is observed along the series Al–Ga–In.

Ouladdiaf and co-workers [2] measured the thermal variation of the lattice parameters  $a$  and  $c$  of  $\text{Pd}_2\text{TiIn}$ . They observed a discontinuity at 92 K (figure 3 in [2]). The present self-consistent band calculations indicated that a cubic structure was more stable than a tetragonal one ( $c/a = 0.989$ ) for  $a = 12.075$  au. (This value of the lattice parameter corresponds to a region of the discontinuity [2].) We did not observe a significant difference between the density of states for tetragonal and cubic structures.

The band structures of  $\text{Pd}_2\text{TiAl}$ ,  $\text{Pd}_2\text{TiGa}$  and  $\text{Pd}_2\text{TiIn}$  are plotted in figure 4(a)–(c). They can be useful for interpreting photoemission experiments.

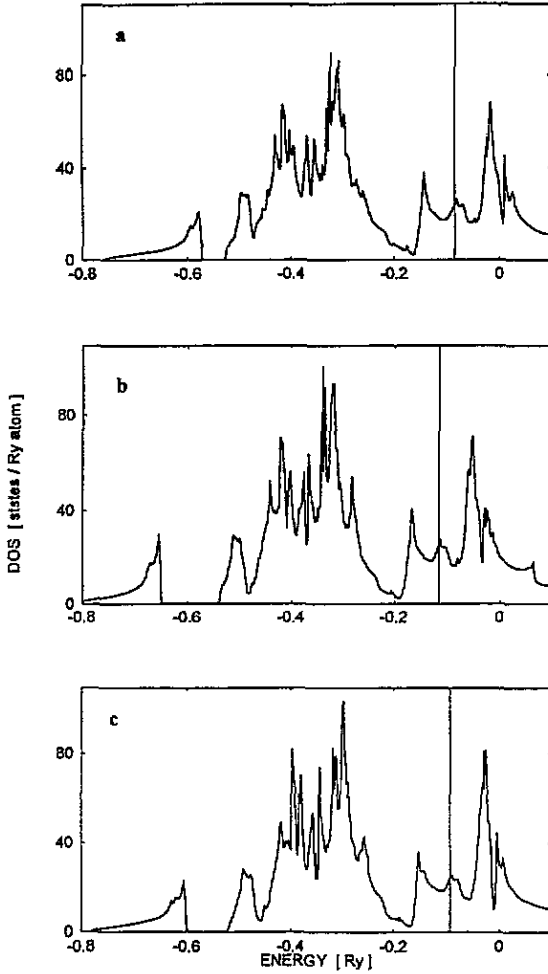


Figure 1. Plot of the total density of states for  $Pd_2TiAl$  (a),  $Pd_2TiGa$  (b) and  $Pd_2TiIn$  (c) alloys. The Fermi level is indicated by the vertical line.

Our self-consistent band structure calculations based on the LSD approximation and TB LMTO method indicate that there is no magnetic moment, neither on Ti nor on Pd in  $Pd_2TiX$  alloys, for  $X=Al, Ga, In$ . The band structure calculations do not support the experimental results [1].

Because of this disagreement the problem of magnetism in  $Pd_2TiX$  alloys was also studied in terms of the extended Stoner model [8–10]. The starting point for the model is the paramagnetic density of states and the rigid-band assumption. The stability of the paramagnetic state is investigated by comparing its magnetic contribution to the total energy with the energy of a magnetic state obtained by shifting  $m/2$  electrons from the down-spin subband to the up-spin subband. The change of the band energy is conveniently expressed in terms of the function  $N(m)$ , defined as [8]

$$N(m) = m / (E_{F+} - E_{F-}) \quad (1)$$

and referred to as the averaged DOS. Here  $E_{F\sigma}$  are determined by the conditions [8]

$$\int_{E_F}^{E_{F\sigma}} n(E) dE = \sigma m / 2 \quad (2)$$

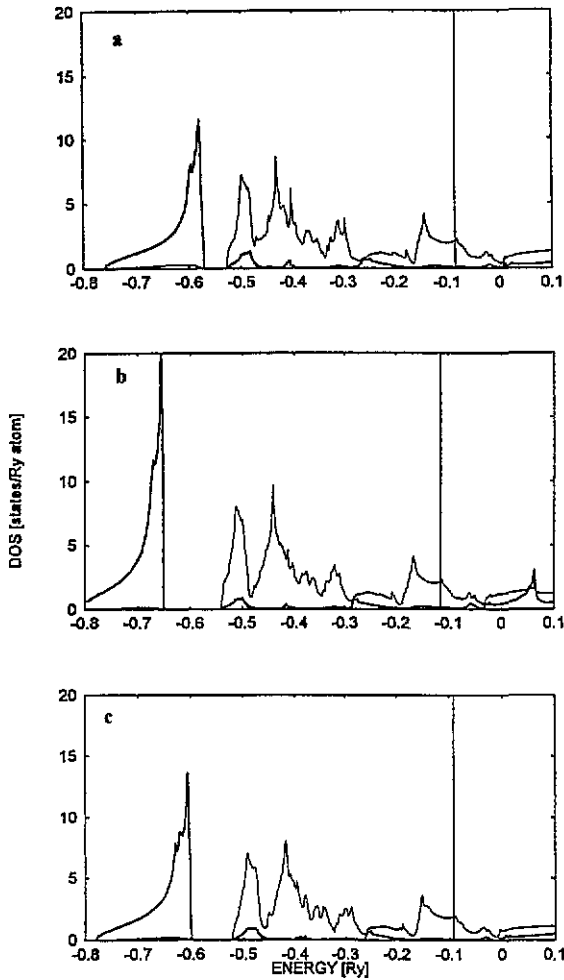


Figure 2. The partial density of states for s (thick curve) and p (thin curve) states for X = Al (a), Ga (b) and In (c) in Pd<sub>2</sub>TiX.

and  $\sigma = \pm$ . The magnetic contribution to the total energy,  $E_m$ , is given by [8]

$$E_m = \frac{1}{2} \int_0^m \frac{m}{N(m)} dm - \frac{1}{4} I m^2 \quad (3)$$

where  $I$  is the effective Stoner integral and  $-\frac{1}{4} I m^2$  represents the interaction energy. The condition for the existence of a ferromagnetic phase is obtained by minimizing the magnetic energy  $E_m$  with respect to  $m$  [8–10]. The condition for a minimum has a form resembling the Stoner criterion:

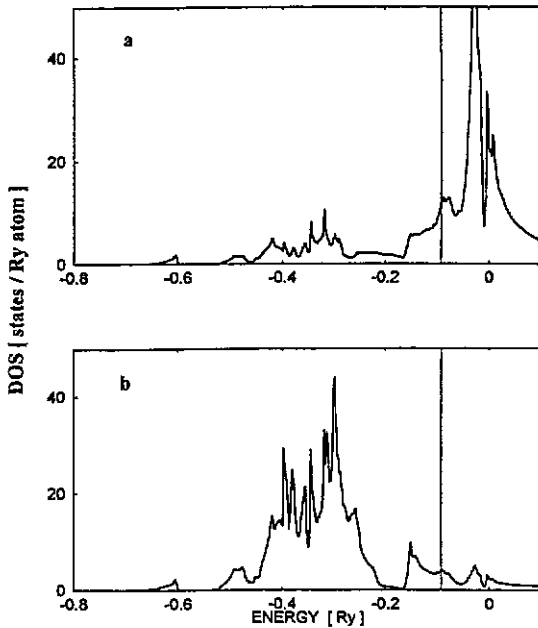
$$N(m)I = 1 \quad (4)$$

where  $I$  is the effective Stoner integral. The stability condition is  $d^2 E_m / dm^2 > 0$  or, equivalently,  $dN(m)/dm < 0$ . It is also necessary to have  $E_m < 0$  for a stable ferromagnetic state, otherwise the ferromagnetic state is metastable [8–10].

In figure 5 we plot the dependence of the averaged DOS  $N(m)$  on the magnetic moment  $m$ , for Pd<sub>2</sub>TiAl (a), Pd<sub>2</sub>TiGa (b) and Pd<sub>2</sub>TiIn (c) alloys.

**Table 1.** The number of electrons on orbitals, charge transfer and the lattice constants of  $Pd_2TiX$ .

X	Cubic Al <sup>a</sup>	Cubic Ga <sup>b</sup>	Cubic In <sup>c</sup>	Tetragonal In <sup>d</sup>
Pd-s	0.500	0.481	0.508	0.500
Pd-p	0.458	0.428	0.452	0.456
Pd-d	8.402	8.434	8.491	8.493
Pd-DQ	-0.641	-0.658	-0.550	-0.550
Ti-s	0.614	0.601	0.625	0.612
Ti-p	0.885	0.835	0.863	0.874
Ti-d	2.612	2.620	2.652	2.665
Ti-DQ	0.111	0.056	0.140	0.150
X-s	1.244	1.406	1.289	0.622
X-p	2.145	2.204	2.042	2.036
X-d	0.780	0.650	1.289	0.634
X-DQ	1.170	1.260	0.960	0.950

<sup>a</sup>  $a = 11.95$  au.<sup>b</sup>  $a = 11.98$  au.<sup>c</sup>  $a = 12.08$  au.<sup>d</sup>  $a = 12.13$  au.**Figure 3.** The PDOS for d states of Ti (a) and Pd (b) in  $Pd_2TiIn$ .

For all  $Pd_2TiX$  systems considered, the condition  $dN(m)/dm < 0$  is satisfied in two intervals of  $m$ . First, for  $m$  in the range  $0.08\mu_B < m < 1.6\mu_B$  and second, for  $m > 3\mu_B$ . In the first range, single stable ferromagnetic solutions can exist for appropriate values of the effective Stoner parameter  $I$ . For higher values of  $I$ , either two solutions (low-moment and high-moment) or a single high-moment solution would be admissible by the condition  $dN(m)/dm < 0$ . However, the high-moment solution would correspond to  $m > 3\mu_B$ . In order to justify disregarding high-moment states with  $m > 3\mu_B$ , calculations of the local moment on Ti atoms were undertaken for an expanded lattice parameter. In many metals

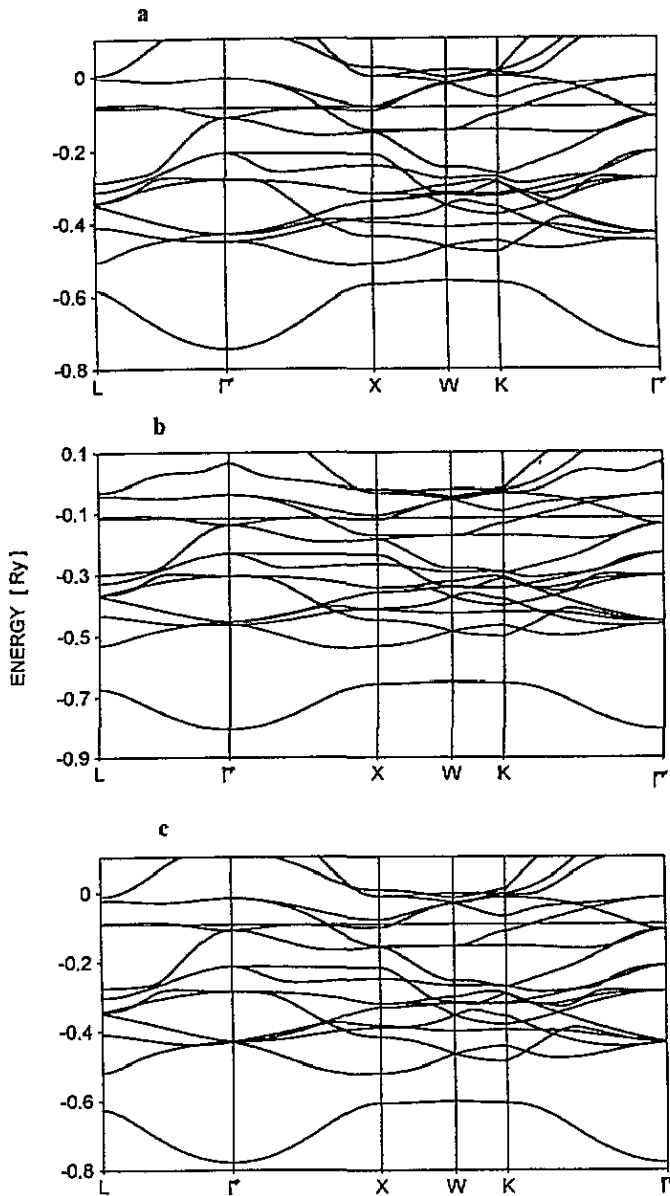


Figure 4. The band structure of  $\text{Pd}_2\text{TiAl}$  (a),  $\text{Pd}_2\text{TiGa}$  (b),  $\text{Pd}_2\text{TiIn}$  (c).

and alloys the magnetic moment depends on the lattice parameter and the local environment. Tripathi and co-workers [11] and Chen and co-workers [12] studied the magnetic moment in FCC rhodium and palladium as a function of the lattice parameter. They found a critical value of the lattice parameter for which the magnetic moment on Rh ( $a > 8$  au) and Pd ( $a > 7.7$  au) appeared. We performed a self-consistent spin-polarized band calculation for different hypothetical lattice parameters larger than the equilibrium value. (The equilibrium or experimental lattice parameters of  $\text{Pd}_2\text{TiX}$  are  $a_{\text{Al}} = 6.322 \text{ \AA}$  [3],  $a_{\text{Ga}} = 6.340 \text{ \AA}$  and  $a_{\text{In}} = 6.39 \text{ \AA}$  (cubic) [2], and  $a_{\text{In}} = 6.42 \text{ \AA}$  and  $c/a = 0.986$  (tetragonal) [2]).

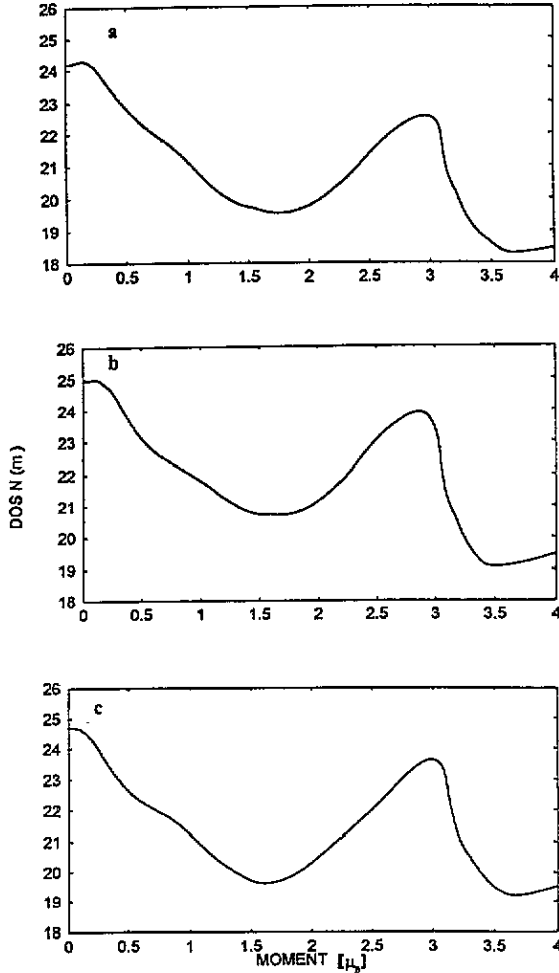


Figure 5. The function  $N(m)$  for  $X = Al$  (a),  $Ga$  (b) and  $In$  (c).

The calculations were made for  $Pd_2TiX$  ( $X = Al$  and  $In$ ) alloys and  $Ti$  with an  $L2_1$ -type structure. In the case of  $Ti$  we considered eight BCC structures. In figure 6 we plot the local magnetic moment on  $Ti$  against lattice parameter. We observe a magnetic moment on  $Ti$  for a lattice parameter  $a > 6.8 \text{ \AA}$ . The local magnetic moments on  $Pd$  and  $X$  atoms were small ( $m_{Pd,X} < 0.01\mu_B$ ). We estimated that a magnetic moment on  $Ti$ ,  $m_{Ti} > 0.2\mu_B$ , existed when the distance between the titanium atoms was  $d_{Ti-Ti} > 3.5 \text{ \AA}$  and each  $Ti$  atom had eight nearest neighbours. The magnetic moment on  $Ti$  atoms builds up, starting from  $a = 6.7 \text{ \AA}$ , and attains a value close to  $2\mu_B$ , as one would expect for an isolated atom at  $a > 8 \text{ \AA}$ . No magnetic moment appears on  $Pd$  irrespective of the value of  $a$ .

A large moment on  $Ti$  is therefore inconsistent with the calculations for expanded interatomic distances exhibited in figure 6. Furthermore, there is no experimental evidence suggesting an existence of low- and high-moment states in the systems considered. The self-consistent spin-polarized band calculations for the Heusler alloys containing  $Ti$  has shown that the magnetic moment on  $Ti$  is small [13–16], if it exists at all. Therefore, we argue that the case of two solutions can be discarded and a magnetic state is only possible if the values of the effective Stoner parameter  $I$  are in the ranges 0.041–0.044 Ryd, 0.040–0.041 Ryd and



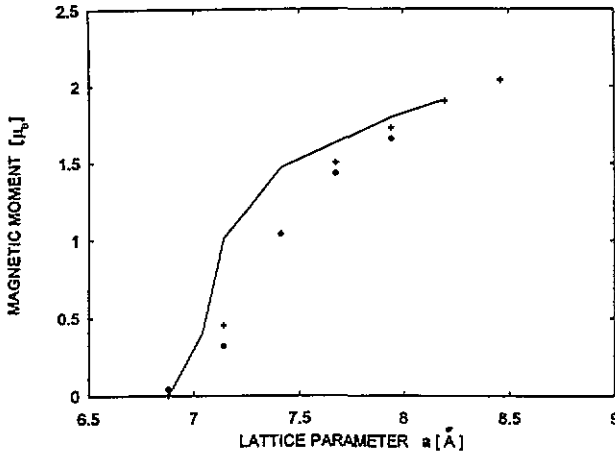


Figure 6. Magnetic moment of Ti in  $\text{Pd}_2\text{TiX}$  alloys for  $X = \text{Al}$  (crosses), and  $\text{In}$  (dots). The full curve represents the results for Ti in an  $L2_1$ -type structure.

0.040–0.042 Ryd for  $X = \text{Al}, \text{Ga}, \text{In}$  in  $\text{Pd}_2\text{TiX}$ , respectively.

We now study the situation for low  $m$  in more detail. The discussion is restricted by the fact that precise values of the effective Stoner parameter  $I$  for alloys, even ordered, are not known. Some indirect arguments must therefore be used. Suppose that for a given system  $\text{Pd}_2\text{TiX}$  the actual value of the parameter  $I$  lies within the range  $I_{\min} < I < I_{\max}$ , so that a ferromagnetic solution is possible. We can thus calculate the magnetic energy  $E_m$  (equation (3)), to check if  $E_m < 0$  as required for a stable state. In figures 7(a)–(c) plots of  $E_m$  against  $m$  are given for a few values of  $I$  from the range  $I_{\min} < I < I_{\max}$ . As is evident from the figure 7(b),  $E_m$  is positive for Ga for any value of  $I$  in that range, therefore one can definitely state that no stable ferromagnetic state exists for  $\text{Pd}_2\text{TiGa}$ . For  $X = \text{Al}$  or  $\text{In}$ , negative values of  $E_m$  are possible but an independent estimate of the actual value of  $I$  is necessary. For that purpose one can use the formula for  $I$  proposed by Jaswal [17]

$$I = \sum_R \left( \frac{N_R(E_F)}{N(E_F)} \right)^2 I_R \quad (5)$$

where  $N_R(E_F)$  and  $N(E_F)$  are the partial and total density of states and  $I_R$  is the Stoner parameter for the  $R$  atom. In our systems there are no d states for  $X = \text{Al}, \text{In}$  so that  $I_X \approx 0$ ,  $N_X(E_F) = 0$ , but only values of  $I_{\text{Pd}}$  and  $I_{\text{Ti}}$  enter into (5). Andersen and co-workers [18] found that, for Pd,  $I_{\text{Pd}} = 0.053$  Ryd. Using this value in (5) and requiring that the left-hand side,  $I$ , be within the range  $I_{\min} < I < I_{\max}$ , specified by figures 7(a), (c), we should assume for  $I_{\text{Ti}}$  a value between 0.085–0.091 Ryd. Such a value of  $I_{\text{Ti}}$  seems far too large to be plausible, compared with the data obtained for  $I_{\text{Ti}}$  in other systems:  $I_{\text{Ti}} = 0.065$  Ryd in  $\text{Co}_2\text{TiSn}$  [16] and  $I_{\text{Ti}} = 0.05$  Ryd in FCC Ti [19]. The conclusion is that none of the  $\text{Pd}_2\text{TiX}$  systems studied exhibits a stable ferromagnetic solution.

#### 4. Conclusions

The aim of the present paper was to shed some light on an apparent inconsistency in existing experimental data on magnetic properties of the Heusler alloys  $\text{Pd}_2\text{TiAl}$  and  $\text{Pd}_2\text{TiIn}$ . Self-consistent spin-polarized TB LMTO calculations have shown that the  $\text{Pd}_2\text{TiX}$  ( $X = \text{Al}, \text{Ga}$

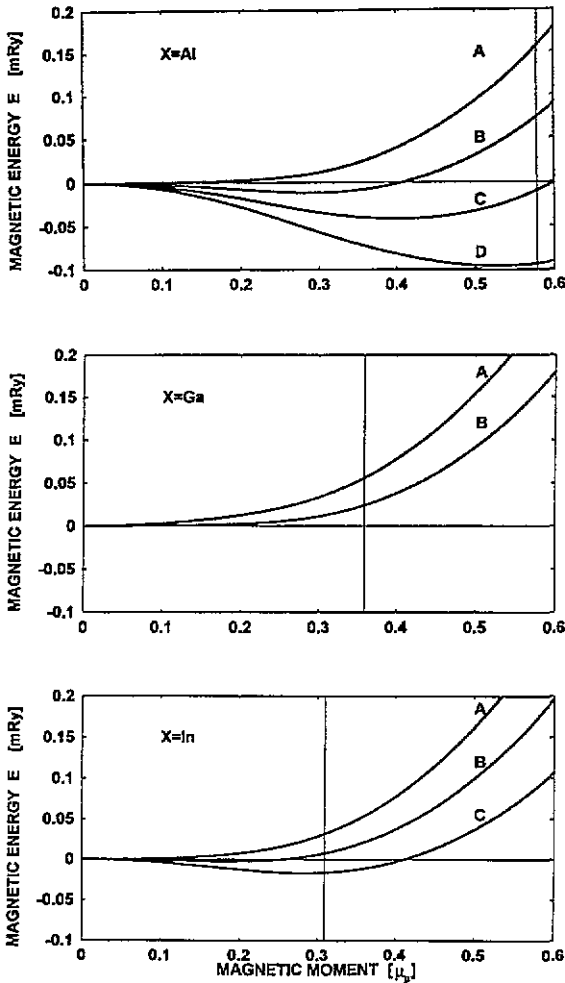


Figure 7. Magnetic energy  $E_m$  against magnetic moment for  $X = Al$ :  $I = 0.041$  Ryd (A),  $I = 0.042$  Ryd (B),  $I = 0.043$  Ryd (C), and  $I = 0.044$  Ryd (D);  $X = Ga$ :  $I = 0.040$  Ryd (A) and  $I = 0.041$  Ryd (B);  $X = In$ :  $I = 0.040$  Ryd (A),  $I = 0.041$  Ryd (B) and  $I = 0.042$  Ryd (C). The vertical line denotes the maximum value of the magnetic moment for which a single solution exists (see text).

and In) alloys are not ferromagnetic, having a zero magnetic moment within a computational uncertainty of  $\Delta m = \pm 0.001 \mu_B$ . This conclusion was corroborated by an analysis based on the extended Stoner model. An instability of the paramagnetic state with respect to hypothetical antiferromagnetic states was not studied.

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