Magnetic properties of tetragonal Pd$_3$Mn

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Abstract. Self-consistent linear muffin-tin orbital spin-polarized calculations were carried out for the tetragonal phase of Pd$_3$Mn. The most stable solution is the antiferromagnetic solution with no magnetic moment on Pd sites. This is in accordance with the most recent neutron diffraction results.

1. Introduction

Pure palladium is strongly paramagnetic. Its properties are substantially altered by addition of different amounts of 3d metals. Iron or cobalt leads to ferromagnetism, while alloying with chromium or manganese increases the antiferromagnetic tendencies of the system (Cable *et al* 1962). Most interesting of these compounds is Pd$_3$Mn. Besides antiferromagnetism, spin-glass freezing in the disordered phase (Rashid and Sellmuer 1984) and mictomagnetism (Chakrabarti 1974), were also investigated in this compound.

Pd$_3$Mn is an interesting compound because of its suitability for hydrogen absorption; indeed this compound is one of the best hydrogen containers. When hydrogen is dissolved in the disordered Pd$_3$Mn phase it can induce a disorder–order transition at elevated temperatures. This transition will not occur at measurable rates in the absence of hydrogen (Flanagan *et al* 1986). Moreover, the hydrogen-induced order was found to be different from the order (Ag$_3$Mg type) resulting after high-temperature annealing in the absence of hydrogen. The mechanism for this hydrogen-induced ordering is as yet unknown and detailed first-principles electronic structure calculations of this system could shed some light on this interesting problem.

Neutron diffraction and magnetic susceptibility measurements were performed on Pd$_3$Mn in both completely ordered and partially disordered phases (Cable *et al* 1962, Krén *et al* 1970, 1972). The antiferromagnetic configuration of Pd$_3$Mn was confirmed in the range 23–30 at.% Mn.

In contrast to relatively detailed experimental investigations of Pd$_3$Mn, theoretical work devoted to this compound has been restricted to electronic structure calculations for the paramagnetic phase and succesive Stoner analysis in order to predict the possibility of magnetic ordering in this compound (Jaswal 1984, Nautiyal and Auluck 1989). These calculations were performed for the simplest Cu$_3$Au structure.

Our aim in this paper is to fill the gap in theoretical investigations of this interesting compound. As a first step we carried out spin-polarized electronic structure calculations for the experimentally observed structure. The present investigations

were stimulated by recent experimental investigations of the crystal and magnetic structures of tetragonal Pd_3Mn and Pd_3MnD_x (Rodić *et al* 1989a, 1990, Ahlzén *et al* 1989), as part of a series of investigations of hydrides. These investigations were based on neutron powder diffraction measurements from 10 to 295 °K and encompassed both pure hydrides and the influence of hydrogenation processes on the crystal and magnetic structures.

In this work we are especially concerned with the most stable antiferromagnetic structure of Pd_3Mn and comparison of theoretical with existing experimental results. The layout of this paper is as follows. Firstly we describe calculational details specific to this compound. In section 3 we present resulting densities of states for the most stable antiferromagnetic structure. To conclude the paper, we discuss agreement between theoretical and experimental results.

2. Details of the calculation

The self-consistent electronic structure calculations were done for Pd_3Mn in several possible antiferromagnetic states. The bands were calculated using the spin-polarized version of the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (Andersen 1975, Skriver 1984). The calculations are semi-relativistic, with mass–velocity and Darvin terms included in the solution of the Dirac equation but with the spin–orbit term omitted. The exchange–correlation potential used in our calculations is the von Barth–Hedin potential (von Barth and Hedin 1972). The initial atomic charge densities were calculated using standard Hartree–Fock–Dirac programs with initial configuration core $+ 4d^{10}$ for palladium and core $+ 3d^5 4s^2$ for manganese. A frozen-core approximation was used; we iterated to self-consistency on valence electrons only.
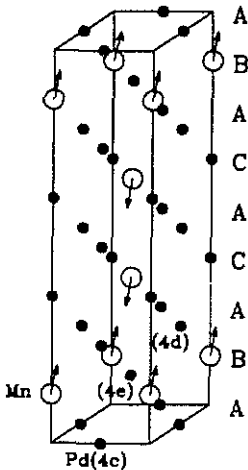

Figure 1. The unit cell content of tetragonal Pd_3Mn. *The spin directions* of the manganese atoms are marked with arrows. Throughout the text we have also used the shortened notation Pd-1 for palladium atoms at 4(c) and 4(e) sites and Pd-2 for palladium atoms at 4(d) sites.

The ideal crystal structure of tetragonal Pd_3Mn is isostructural with the Al_3Zr type structure (Brauer 1939), which belongs to the space group $I4/mmm$. this structure can be built up from three different layers perpendicular to the c axis. Layer A *consists of palladium atoms only, whereas layers B and C contain both palladium and*

manganese atoms. The stacking order in one cell, shown in figure 1, is A B A C A C A B A. Our electronic structure calculations were done using Skriver's computer code. The spheres around the atoms were taken to be of equal size with their radii equal to $S = 2.882802$ a.u. This value of sphere radius corresponds to cell parameters $a = 7.376794$ a.u. and $c \approx 4a$ (Rodić *et al* 1989b). We have used 45 k-points in the irreducible wedge of the Brillouin zone.

3. Results and discussion

Table 1. Atomic positions and types for Pd$_3$Mn. The atomic coordinates are given in units of a. The crystal structure is $I4/mmm$, the lattice constant being $a = 7.376794$ for x and $c = 29.507176$ for y.

Atom	Type	x	y	z
Mn	1	0.0	0.0	0.5
Mn	1	0.0	0.0	3.5
Mn	2	0.5	0.5	1.5
Mn	2	0.5	0.5	2.5
Pd	1	0.5	0.0	0.5
Pd	1	0.0	0.5	0.0
Pd	1	0.5	0.5	0.5
Pd	1	0.5	0.5	3.5
Pd	2	0.5	0.0	1.0
Pd	2	0.0	0.5	1.0
Pd	2	0.5	0.0	3.0
Pd	2	0.0	0.5	3.0
Pd	3	0.0	0.0	1.5
Pd	3	0.5	0.0	2.0
Pd	3	0.0	0.5	2.0
Pd	3	0.0	0.0	2.5

Band structure calculations for Pd$_3$Mn with 16 atoms per unit cell were done within the local spin-density approximation. The crystal structure was $I4/mmm$ and the lattice constants were $a = 7.376794$ and $c = 29.507176$. The ionic types and positions used in this study are listed in table 1. The basic collinear antiferromagnetic arrangement of the Mn moments was established in the experimental papers already mentioned and so it is natural to take two manganese types in our LMTO calculations. Furthermore, the probabilities of finding an ordered moment on different palladium sites are not the same. Every Pd atom has four Mn atoms among its nearest neighbours, but while Mn moments surrounding the Pd atoms on 4(c) and 4(e) sites are parallel, resulting in a polarizing exchange field on the Pd moments, those around 4(d) sites compensate each other and the exchange field is zero. Owing to the fact that palladium atoms 4(c) and 4(e) have an almost identical neigbourhood (figure 1), throughout the text we use the following notation: Pd-1 for palladium atoms at 4(c) and 4(e) sites and Pd-2 for palladium atoms at 4(d) sites.

The magnetic moments of palladium in the Pd$_3$Mn alloy have been considered by earlier workers. Old neutron diffraction measurements on polycrystalline samples of 75% Pd–25% Mn alloy (Cable *et al* 1962) gave atomic magnetic moments $(4.0 \pm 0.2)\mu_B$ per Mn and $(0.2 \pm 0.1)\mu_B$ per Pd. Krén *et al* (1972) found values $(4.1 \pm$
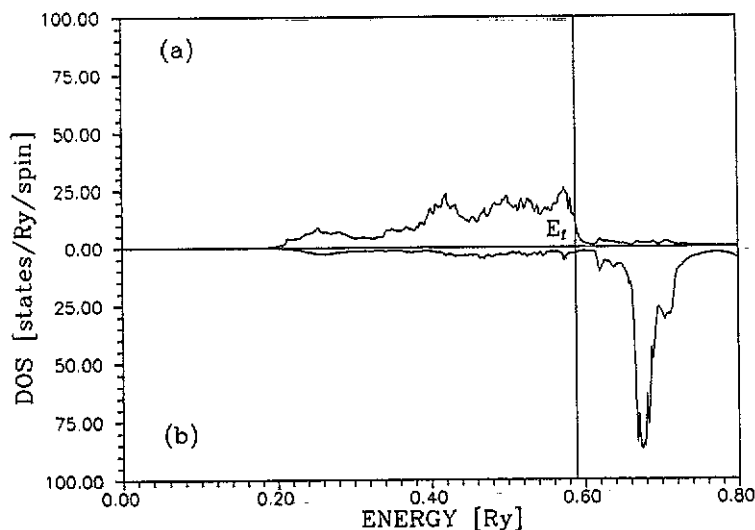
Figure 2. The self-consistent 3d state density of Mn-1 for majority (*a*) and minority (*b*) spin directions in antiferromagnetic Pd_3Mn. Magnetic moments for Pd atoms on 4(c) and 4(e) sites are coupled antiparallel to neighbouring Mn moments.
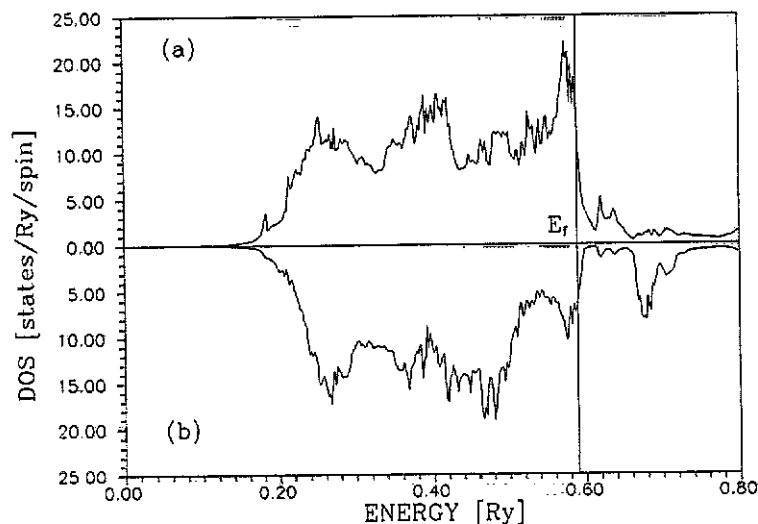

Figure 3. Density of 3d states for Pd-1 for majority (*a*) and minority (*b*) spin directions.

$0.3)\mu_B$ per Mn and $(0.15 \pm 0.03)\mu_B$ per Pd in Pd-1 4(c) and 4(e) positions. Magnetic moments on Pd atoms are coupled antiparallel to neighbouring Mn moments. In other experimental papers (Krén and Kádár 1969, Krén *et al* 1970, Rodić *et al* 1989a,1990) no magnetic moment was found on Pd sites.

We tried to investigate this controversy carefully in our calculations. We started our calculations for antiferromagnetic Pd_3Mn with an antiparallel polarizing exchange field on Pd-1 sites. The magnetic moment on Pd-2 sites was taken to be zero, from plausible symmetry arguments. The density of d states for this case for manganese
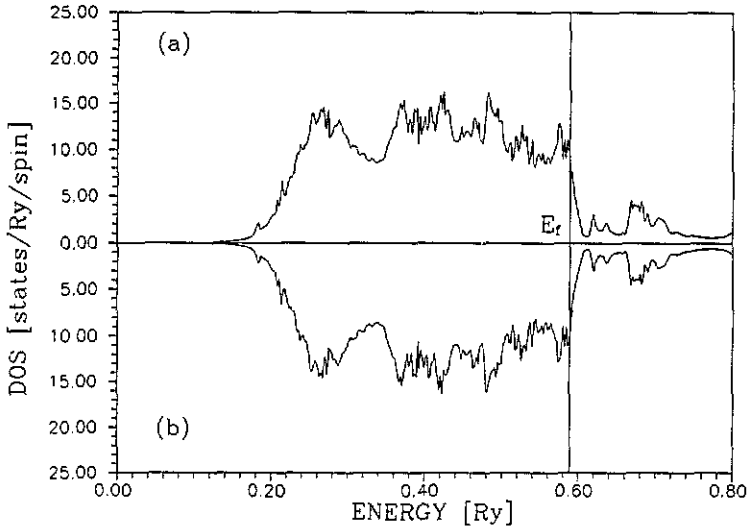
Figure 4. Density of 3d states for Pd-2 for majority (*a*) and minority (*b*) spin directions.

for and Pd-1 and Pd-2 sites for the majority and minority spin directions are given in figures 2–4. The contribution of s and p electrons to the density of states on Mn and Pd is very small in the energy region several eV below the Fermi level and d electrons are the only important electrons for explanation of the main properties of Pd₃Mn alloy. Characteristic strong hybridization between d electrons of manganese and palladium is also evident. This hybridization produces significant changes in the density of manganese d states for the majority spin direction. Very little polarization is found at palladium sites. We can see a large splitting between the centres of manganese d bands. Let us also note that the manganese majority spin band width has been significantly increased. In table 2 we summarize quantities resulting from our calculations in this case. These are the occupation numbers, densities of states, band splittings and contributions to the spin magnetic moment decomposed by site, angular momentum quantum number l and spin quantum number s. We see from this table that the magnetic moment is mainly localized on manganese sites, while it is small for Pd sites.

During iteration to self-consistency, we started with a small initial splitting between majority and minority spin states on Pd-1 4(c) and 4(e) sites antiferromagnetically coupled to the surrounding manganese atoms. One should check carefully that the system relaxes to the ground state rather than to a metastable state. The convergence to the ground state given in table 2 and figures 2–4 was very slow and more than five big iteration loops (a complete LMTO band structure calculation was performed in each big iteration) were necessary to get a stable self-consistent solution.

We further attempted to obtain a self-consistent solution for antiferromagnetic Pd₃Mn, but in this second model we assume that the magnetic moments of Pd atoms at both Pd-1 and Pd-2 sites are aligned parallel to the moment of manganese. Self-consistent results are summarized in table 3, which shows a magnetic moment of $0.181\mu_B$ at the Pd-1 site but no moment at Pd-2. This value is in excellent agreement with the experimental magnetic moment at the respective Pd sites as reported earlier (Cable *et al* 1962, Krén *et al* 1972). Note the difference in the type

Table 2. Data from self-consistent band structure calculations for antiferromagnetic Pd_3Mn with zero magnetic moment on all Pd sites. (Here we tried to get self-consistent solutions starting from small finite moments on Pd sites and antiparallel orientation of moments on Pd and neighbouring Mn atoms.)

		Manganese	Palladium 1	Palladium 2
Atomic sphere radius (a.u.)		2.882802	2.882802	2.882802
Occupation per spin per atom	s↑	0.344	0.311	0.320
	s↓	0.294	0.327	0.320
	p↑	0.413	0.340	0.340
	p↓	0.327	0.340	0.340
	d↑	4.562	4.368	4.362
	d↓	0.924	4.360	4.362
Density of states (states/Ryd/atom/spin)	s↑	0.253	0.143	0.181
	s↓	0.332	0.140	0.181
	p↑	0.406	0.374	0.518
	p↓	0.242	0.613	0.518
	d↑	14.680	16.916	10.652
	d↓	3.006	7.045	10.657
Total	↑	15.339	17.433	11.351
	↓	3.580	7.798	11.356
Band splitting (mRyd) $(C_{l\uparrow} - C_{l\downarrow})$	s	−164.9	12.5	0.0
	p	−167.8	12.9	0.0
	d	−195.5	15.6	0.000
Contribution to magnetic moment per atom	s	0.050	-0.016	0.000
	p	0.087	0.000	0.000
	d	3.638	0.009	0.000
Total (μ_B)		3.775	-0.007	0.000

of coupling between manganese and palladium: here we get a self-consistent solution for ferromagnetic coupling while the experimental work mentioned above reported antiparallel exchange coupling between manganese and palladium. In figure 5 we give the density of Pd-1 d states corresponding to this case. This is the most noticeable difference in the density of electronic states relative to the first calculations, in which we obtained a self-consistent solution with no magnetic moment at Pd sites.

In all calculations, we computed the total energy, which indicated that the most stable solution is that with zero magnetic moments on palladium sites.

4. Concluding remarks

The results of local spin-density functional LMTO band structure calculations for antiferromagnetic Pd_3Mn in the tetragonal structure have been presented. We have carefully investigated the possibility of there being a magnetic moment on Pd sites.

The exchange-type mechanism for the appearance of ordered Pd moments induced by neighbouring Mn moments was suggested in the first neutron diffraction investigation of polycrystalline samples of 75% Pd–25% Mn alloy (Cable *et al* 1962). A small magnetic moment on Pd atoms (0.2 ± 0.1)μ_B was reported there, but not confirmed later (Krén and Kádár 1969, Krén *et al* 1970). Later investigation by the same group (Krén *et al* 1972) showed a magnetic moment of $(0.15 \pm 0.03)\mu_B$ in Pd-1
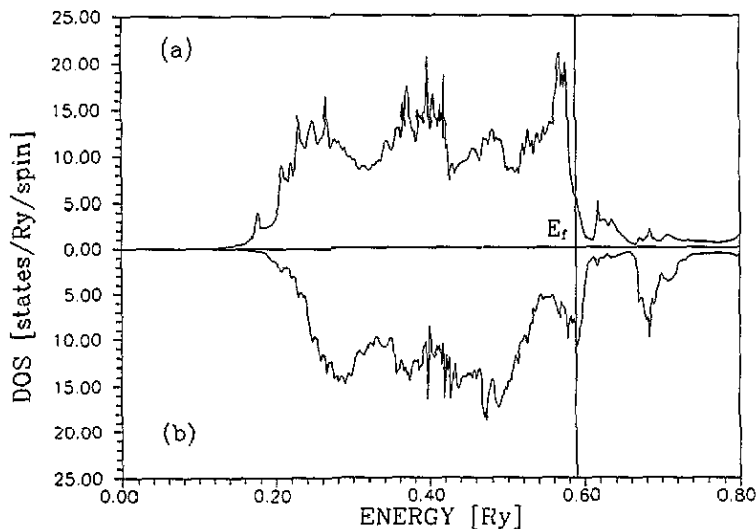
Figure 5. Density of Pd-1 3d states for majority (*a*) and minority (*b*) spin directions. This solution for antiferromagnetic Pd₃Mn gives $0.181\mu_B$ on 4(c) and 4(e) sites and ferromagnetic exchange interaction with neighbouring Mn atoms.

4(c) and 4(e) positions coupled antiparallel to manganese moments of $(4.1 \pm 0.3)\mu_B$. This is somewhat surprising, since the analogous ordered alloys Ni₃Mn and Pt₃Mn are not only ferromagnetic but have Curie temperatures increasing with increasing long-range order, indicating that Ni–Mn and Pt–Mn near-neighbour interactions are ferromagnetic.

Recent neutron diffraction experiments (Rodić *et al* 1989a, 1990) gave a magnetic moment on Mn sites only. These moments are ordered antiferromagnetically. They found $(5.2 \pm 0.1)\mu_B$ per Mn atom at 10 °K and $4.7\mu_B$ at 70 °K. The angles of magnetic moments with respect to the tetragonal *c* axis for the respective temperatures are 10° and 12°. The authors of this latest experimental investigation carefully analysed the possibility of finding a magnetic moment on Pd sites. If no constraint were put on the occupation numbers, a small magnetic moment of $0.15\mu_B$ per Pd atom aligned along the *c* axis was found. However, the occupation numbers obtained give a calculated stoichiometric ratio which differs by 3% from the chemical analysis. After introducing the stoichiometric 3 : 1 ratio, the moments on Pd atoms disappeared.

We found that the most stable solution energetically is the antiferromagnetic case with no magnetic moment on Pd sites. These results support the most recent experimental investigations of Rodić *et al* (1990). The magnitude of the magnetic moment at Mn sites of $3.8\mu_B$ obtained theoretically is in quite acceptable agreement with experiment. The most recent experimental results for moments on Mn sites are noticeably higher than earlier experimental values and our theoretical values. The explanation is that the magnetic moment on Pd sites of 4(c) and 4(e) type, seen in some earlier experiments, is due to Mn atoms on Pd sites and non-ideal stoichiometry in the samples measured. We were not able to obtain a stable self-consistent solution with a finite magnetic moment on Pd sites with an antiparallel polarizing exchange field between neighbouring manganese and palladium atoms at 4(c) and 4(e) sites. The only self-consistent solution we could get with magnetic moments on these palla-

Table 3. Data from the band structure calculations for antiferromagnetic Pd_3Mn with ferromagnetic interaction between Mn and Pd sites. We treated 16 atoms per unit cell.Because of antiferromagnetic ordering of Mn atoms and between Pd-1 and Pd-3 we do not give results for second Mn type and third Pd type atoms. Up (down) spin results for these atoms are only interchanged with down (up) results for Mn and Pd 1 given in the table.

		Manganese	Palladium 1	Palladium 2
Atomic sphere radius (a.u.)		2.881077	2.881077	2.881077
Occupation per spin per atom	$s\uparrow$	0.337	0.310	0.320
	$s\downarrow$	0.303	0.327	0.320
	$p\uparrow$	0.397	0.336	0.341
	$p\downarrow$	0.351	0.348	0.341
	$d\uparrow$	4.632	4.469	4.362
	$d\downarrow$	0.834	4.259	4.361
Density of states (states/Ryd/atom/spin)	$s\uparrow$	0.162	0.117	0.131
	$s\downarrow$	0.226	0.087	0.130
	$p\uparrow$	0.215	0.342	0.521
	$p\downarrow$	0.279	0.526	0.521
	$d\uparrow$	5.393	7.216	9.959
	$d\downarrow$	3.101	17.770	9.828
Total	$\uparrow$	5.770	7.675	10.611
	$\downarrow$	3.606	18.383	10.479
Band splitting (mRyd) $(C_{i\uparrow} - C_{i\downarrow})$	s	-99.4	-0.513	-0.013
	p	-104.3	-0.124	0.014
	d	-236.6	-7.42	-0.031
Contribution to magnetic moment per atom	s	0.034	-0.017	0.000
	p	0.046	-0.012	0.000
	d	3.798	0.210	0.001
Total (μ_B)		3.878	0.181	0.001

dium sites is the solution with parallel moments on neighbouring manganese atoms, but this solution is energetically less favourable than the solution with no magnetic moment on palladium sites.

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