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THE CRYSTAL AND MAGNETIC STRUCTURE OF TETRAGONAL Pd_3Mn

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The crystal and magnetic structures of tetragonal Pd_3Mn have been analysed by Rietveld profile refinements of neutron powder data obtained at 10, 70 and 295 K. The tetragonal modification of Pd_3Mn has the unit cell dimensions $a = 3.9036(3)$ Å, $c = 15.624(2)$ Å at 295 K; $a = 3.8934(4)$ Å, $c = 15.586(3)$ Å at 70 K; $a = 3.8806(8)$ Å, $c = 15.545(3)$ Å at 10 K. The magnetic structure is colinear antiferromagnetic below $T_N = 200(2)$ K. The direction of the magnetic moment on the manganese atoms forms an angle of 11(1)° with the tetragonal axis.

1. INTRODUCTION

ABOVE a critical temperature of approximately 800 K, Pd_3Mn crystallizes in a disordered f.c.c. structure. Below this temperature an ordered tetragonal structure of the Al_3Zr-type is formed. However, the ordering reaction is slow and a fully ordered sample is difficult to obtain.

An ordering of the magnetic moments to a colinear antiferromagnetic structure occurs below approximately 200 K. The Néel temperature T_N is a function of the long-range order parameter. Cable *et al.* [1] have found $T_N = 170$ K in a Pd_3Mn alloy with $S = 0.63$ and Krén *et al.* [2] report $T_N = 195$ K for $S = 0.90$.

Cable *et al.* [1] found the magnetic moments at 78 K to be $4.0(2)\,\mu_B$/Mn atom and $0.2(1)\,\mu_B$/Pd atom, pointing in a direction perpendicular to the c-axis. Krén *et al.* [2] and Krén and Káddár [3] have observed the direction of the moments to change with composition. Less than 25 at % Mn gives a spin direction parallel to the c-axis, $\phi_c = 0°$, whereas more than 25 at % Mn gives a spin direction perpendicular to the c-axis, $\phi_c = 90°$. In the 25 at % Mn alloy, the angle ϕ_c is independent of temperature but dependent of the long-range order: $S = 0.90$ results in $\phi_c = 8°$ and $S = 0.45$ leads to $\phi_c = 55°$. In the first case (Pd_3Mn, $S = 0.90$) the Mn magnetic moment at 78 K was found to be $4.1(3)\,\mu_B$; no magnetic moments was considered on the Pd atoms.

All phases of Pd_3Mn have been reported to absorb hydrogen [4]. The present study is part of our series of investigations of metal hydrides. The aim of these investigations is to study the influence of the hydrogenation process on the crystal and magnetic structures. In the present paper, we report a careful characterization of a Pd_3Mn sample before hydrogenation. This characterization is necessary due to the variety of crystalline and magnetic structures which can be found in the system.

2. EXPERIMENTAL

The alloy was prepared by high frequency melting in an argon atmosphere. The product was crushed and ground to a fine powder. The powder was then heated in vacuum at 740 K for 24 h followed by slow cooling.

The neutron powder diffraction data obtained at 10 K were collected at the Orphée Reactor in Saclay. A computer controlled closed system refrigerator (Displex) with a temperature stability of ±1 K was used. A neutron beam monochromatized from a Cu(1 1 1) single crystal was passing through a collimator system with $\alpha_1 = 14'$ and $\alpha_3 = 10'$ giving a wavelength of 1.066 Å and a neutron intensity of $5 \times 10^6\,cm^{-2}\,s^{-1}$ at the sample position. The powder specimen with a volume of about $1.5\,cm^3$ was contained in an aluminium tube with 6 mm diameter. A

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stepscan was performed in the angular range 2.5–42° with a stepsize of 0.05° in 2θ and a step time of $3\,\mathrm{min\,step}^{-1}$.

The same instrumentation was used for determination of the Néel temperature. The angular range was in this case a few steps around $2\theta = 15.75°$ (1 0 0) scanned at 19 different temperatures between 10 and 295 K.

The 70 and 295 K data were collected at the Swedish research reactor R2 in Studsvik. Two copper (2 2 0) crystals were used in a double monochromator to obtain a monochromatic beam. After collimation ($\alpha_1 = 12'$ and $\alpha_2 = 10'$) the final neutron flux at the specimen was about $10^6\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ at a wavelength of 1.470 Å. A computer controlled multidetector system was used. Five detectors were set at 3.12° intervals and scanned in unison over the complete 2θ-range. The contribution from the different detectors were then summed for each 2θ-step making a calibration of the detector efficiency unnecessary. The scan-ranges were 9.00–116.52° (295 K) and 3.00–116.52° (70 K), both with a step of 0.08° in 2θ. For the 70 K data a Displex CS-1003 closed system was used with a temperature stability of ±2 K.

2.1. *Refinement*

The intensity data was evaluated with the Rietveld method [5]. Atomic coordinates in space group *I4mm*, previously reported [2, 3, 6], were used as starting parameters in the least-squares refinements. Problems with linear dependences between atomic positions indicated an improper choice of space group. Moving the origin 0.125 along the *c*-direction the same atomic arrangement can be described in the centrosymmetric space group *I4/mmm*. As no indication was found of physical properties that could not be described in a centrosymmetric space group the latter was used in the subsequent refinements.

In space group *I4/mmm* the Mn atoms occupy 4*e* positions whereas the Pd atoms occupy 4*c*, 4*d* and 4*e* positions; only the atoms in the 4*e* position has a freedom in the *z*-coordinate. In a partially disordered Pd_3Mn system Mn and Pd atoms also occupy positions dominantly occupied by the other atom. As a chemical analysis of the sample showed no significant deviation from the stoichiometric ratio 3 : 1, full occupation of all Wyckoff's positions was assumed (i.e. $n_{\mathrm{Pd}} + n_{\mathrm{Mn}} = 1$, with $\Sigma n_{\mathrm{Pd}} = 3$ and $\Sigma n_{\mathrm{Mn}} = 1$).

The neutron diffraction technique is very well suited to clarify the disorder problem as the scattering length for Mn is negative $b_{\mathrm{Mn}} = -3.73\,\mathrm{fm}$ as compared to $b_{\mathrm{Pd}} = 5.91\,\mathrm{fm}$.

It was found during the refinements that all Mn temperature factors and the occupation numbers of the manganese atoms in the different "Pd" sites were very similar and a satisfactory agreement could be achieved using a common isotropic B factor and a common occupation number. The same was true for the palladium atoms.

Altogether 13 independent parameters have been used in the last cycles of refinement of the crystal structure; one scale factor, one zero point correction and three parameters for the description of the half width of the peaks. The remaining 8 parameters were two cell parameters (*a*, *c*), two temperature factors (B_{Pd}, B_{Mn}), occupation numbers $n_{\mathrm{Mn}}(4e)$ and $n_{\mathrm{Pd}}(4c, 4d, 4e)$ and two *z*-coordinates (4*e*). At 10 K the thermal parameters were less than one standard deviation from zero and were therefore fixed at this value. The magnetic structure below T_N was described with two additional parameters on the Mn atoms (components of the magnetic moment, parallel and perpendicular to the *c*-axis). The magnetic form factor table for Mn was taken from Watson and Freeman [7] and that for Pd from Moon, Koehler and Cable [8].

The experiments at 295 and 70 K have been carried out twice. The reason was the big discrepancies obtained between the *R*-values calculated on the profile (with an assumed Gaussian peak shape) and those calculated on the integrated intensities column 2 and 4 in Table 1). As can be seen in Fig. 1 the profile does not fit very well in the lower parts of the reflexions and we consider this fact to be a consequence of the disorder. In an attempt to reduce this disorder the sample was reheated in vacuum at 740 K for another 48 h and then slowly cooled. A comparison of the results in Table 1 shows that the discrepancies still remain after the heat treatment.

2.2. *The crystal structure*

The ideal crystal structure of tetragonal Pd_3Mn is isostructural with Al_3Zr [9]. The structure can be described as built up of three different layers perpendicular to the *c*-axis. Layer A consists of only palladium atoms whereas layer B and C contain both palladium and manganese atoms. The stacking order in one unit cell as shown in Fig. 2 is ABACACABA.

The parameters obtained from the crystal structure refinements are given in Table 1. From the occupation numbers we have calculated a long range order parameter S using the formula for a binary alloy [10]. The calculated values shown in Table 1 are not significantly different for different temperatures. The mean value is 0.85(1).

2.3. *The magnetic structure*

A comparison of obtained diffraction data at 10, 70 and 295 K shows that all reflexions found at room

Table 1. Results from the refinements of tetragonal Pd_3Mn

T	R_{nucl}	R_{magn}	R_{prof}	$R_{w.prof}$	a	c	B (Pd)	B (Mn)	n $(Pd)_{4c,d,e}$	n $(Mn)_{4e}$	S	M	ϕ_c	Z (Pd) $(\frac{1}{2}, \frac{1}{2}, z)$	Z (Mn) $(0, 0, z)$
10 K	2.65	3.57	10.78	12.43	3.8806 (8)	15.545 (3)	0.0	0.0	0.958 (2)	0.876 (4)	0.83 (1)	5.2 (1)	10 (1)	0.1276 (4)	0.118 (1)
70 K$^{(bef)}$	5.64	7.71	15.93	19.80	3.8953 (4)	15.594 (3)	0.09 (3)	0.5 (1)	0.966 (3)	0.900 (9)	0.87 (1)	4.7 (1)	12 (1)	0.1272 (6)	0.119 (1)
70 K$^{(aft)}$	4.48	6.11	17.39	19.98	3.8934 (4)	15.586 (3)	0.07 (5)	0.5 (1)	0.960 (3)	0.882 (9)	0.84 (1)	4.5 (1)	12 (1)	0.1264 (6)	0.120 (1)
295 K$^{(bef)}$	5.32	–	16.69	18.67	3.9028 (5)	15.626 (3)	0.38 (3)	0.9 (2)	0.962 (2)	0.888 (8)	0.85 (1)	–	–	0.1227 (5)	0.130 (1)
295 K$^{(aft)}$	4.78	–	14.33	16.33	3.9036 (3)	15.624 (2)	0.48 (5)	1.2 (2)	0.960 (2)	0.880 (6)	0.84 (1)	–	–	0.1227 (5)	0.129 (1)

$^{(bef)}$ and $^{(aft)}$ mean before and after the second head treatment (c.f. refinement).

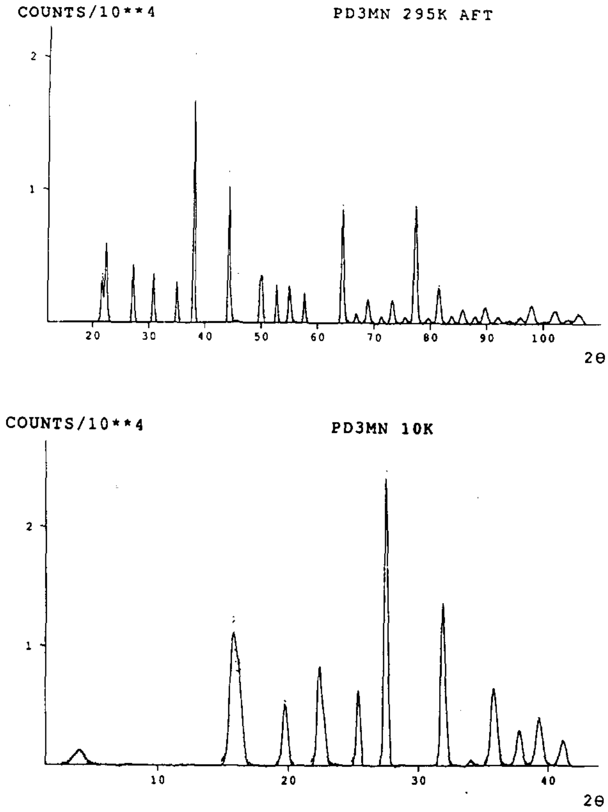

Fig. 1. A plot of observed (dots) and calculated (full line) neutron intensities of tetragonal Pd_3Mn at (a) 295 K, $\lambda = 1.470$ Å and (b) 10 K, $\lambda = 1.066$ Å.

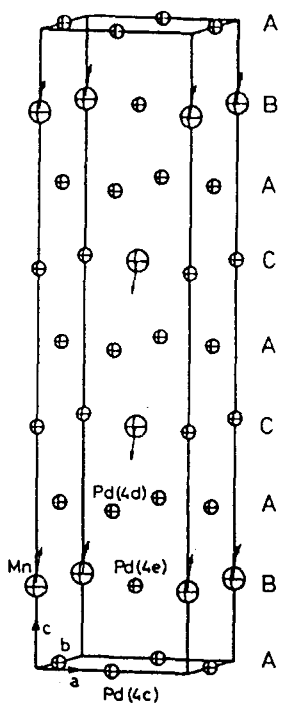

Fig. 2. The contents of the unit cell showing the magnetic moment on the Mn atoms.

temperature can be found in the low temperature data and, if proper care is taken to the thermal smearing, with the same intensity. These reflexions can all be indexed with the given body-centred unit cell having $h + k + l = 2n$. In addition data collected at 10 and 70 K contain some extra reflexions which cannot be found at 295 K. These extra reflexions can be indexed with the same unit cell but having $h + k + l = 2n + 1$, which are forbidden reflexions in space group $I4/mmm$.

A straightforward conclusion, which can explain all these observations, is that reflexions with even sum are nuclear reflexions, whereas reflexions with odd sum are pure magnetic reflexions originating from a colinear antiferromagnetic structure with an antitranslation element $1/2(\mathbf{a} + \mathbf{b} + \mathbf{c})$ characteristic for the $P_I(I_p)$ lattice.

The analysis of magnetic intensities yields a propagation vector $\mathbf{k} = (0, 0, 1)$ and an ordering of the magnetic moments $(+ - - +)$ (cf. Fig. 2). From the refined values of M_x and M_z, the magnetization components perpendicular and parallel to the c-axis, respectively, we can calculate the total magnetic moment and the angle ϕ_c between the c-axis and the direction of the moments (Table 1, columns 13, 14). The obtained values for the magnetization, $\mu = 5.2(1)\,\mu_B$ per Mn atom at 10 K and $4.7(1)\,\mu_B$ at 70 K, are in good agreement with previous results [1, 2, 3, 11]. A slightly smaller value at 10 K than at 70 K has been obtained for the angle ϕ_c, 10° and 12°, respectively. The estimated standard deviation is, however, 1°, so from this study it is not possible to say with any certainty if ϕ_c is temperature dependent or not.

The possibility of magnetic moment on the Pd atoms was carefully investigated. The mechanism for the appearance of ordered Pd moments is a polarization induced by the Mn moments. A small magnetic moment on the Pd atoms has been reported [1] but not always accepted [2, 3]. In a more recent investigation the existence of an ordered moment on the Pd atoms was claimed, but only on the $4c$ and $4e$ sites. The magnetic moments on the $4d$ sites was taken to be zero from plausible symmetry arguments [11].

If no constraint was put on the occupation numbers a small magnetic moment of $0.15\,\mu_B$ per Pd atom aligned along the c-direction was found. However, the obtained occupation numbers give a calculated stoichiometric ratio which differs within 3% from the chemical analysis. After introducing the stoichiometric 3 : 1 ratio, the moments on the Pd atoms

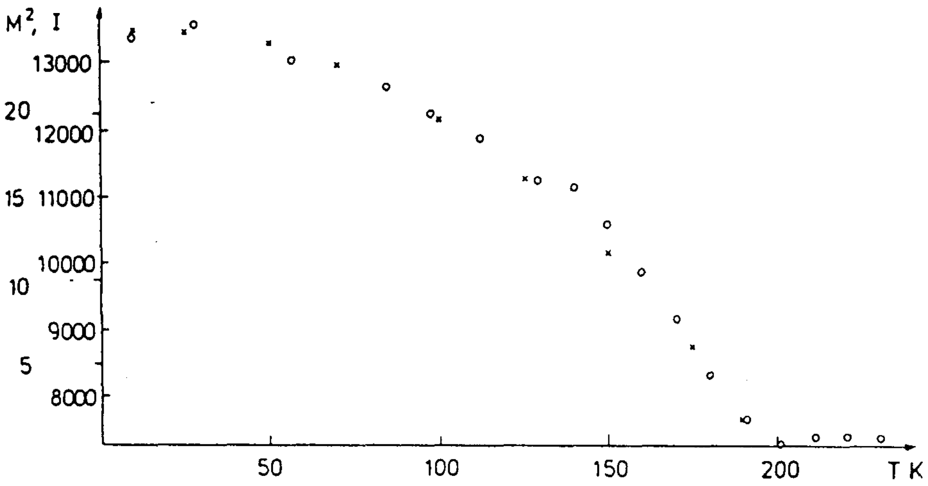

Fig. 3. Observed intensities (circles) for the magnetic (1 0 0) reflexion and a calculated Brillouin behaviour of the magnetization (crosses) vs temperature (the scale between the two curves is arbitrary).

disappeared being only one half of its standard deviation from zero.

The magnetic moments on the disordered Mn-atoms in Pd-sites 4*c* and 4*e* agree with that of the ordered Mn-atoms within one standard deviation. In the final cycles of refinement the magnetic components of all 4*c*, 4*e* Mn atoms were varied with two common parameters. No ordered magnetic moment has been found on the Mn atom in Pd-site 4*d*.

The partial disorder in the structure gives rise to a certain anisotropy in the magnetic interactions. The angle ϕ_c between the spin direction and the *c*-axis has been reported to change with composition. It is reasonable to believe that the degree of disorder has the same effect.

2.4. *The Néel temperature*

In order to determine the temperature at which the magnetic ordering occurs, a stepscan over the magnetic (1 0 0) reflexion was carried out at 19 different temperatures. The result is shown in Fig. 3, where the circles correspond to the observed intensities. From this curve the Néel temperature T_N = 200(2) K was obtained.

To compare the experimental result with theory, a Brillouin curve was calculated [12] using the parameters $S = 5/2$ and $T_N = 200\,K$. The result is shown with crosses in the same diagram as the observed intensities (the scale between the two curves is arbitrary chosen). As can be seen the general form of the two curves is essentially the same.

A more detailed comparison between the observed magnetization and that calculated within a mean field approximation is made by Rodic *et al.* [13].

3. CONCLUSIONS

The results from this work on tetragonal Pd_3Mn at three different temperatures can be summarized as follows:

- The tetragonal crystal structure earlier reported was confirmed.
- The sample was not fully ordered. From the occupation numbers an order parameter $S = 0.85(1)$ was calculated.
- An ordered colinear antiferromagnetic structure was found at low temperatures.
- The Néel temperature was determined to $T_N = 200(2)\,K$.
- The magnetic moment on Mn ($S = 5/2$) was found to be 5.2(1) μ_B at 10 K and 4.7(1) μ_B at 70 K. The magnetization shows a typical Brillouin behaviour.
- The angle between the spin direction and the tetragonal *c*-axis is 10°(1) at 10 K and 12°(1) at 70 K.
- No ordered magnetic moment has been found on the Pd atoms.

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