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Equiatomic Transition Metal Alloys of Manganese

V. On the Magnetic Properties of the PtMn Phase

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X-Ray and neutron diffraction, and magnetic susceptibility measurements of the alloy $Pt_{35}Mn_{65}$ with the CuAuI type crystal structure show an antiferromagnetic arrangement of the magnetic moments with spin quantum numbers $2S_{Mn} = 3.1 \pm 0.2$ and $2S_{Pt} < 0.2$. The moments of nearest-neighbour Mn atoms are arranged antiparallel within the (001) planes. The alloy has a Néel temperature of ~710°K and exhibits weak ferromagnetism below ~250°K.

In continuation of our examination of transition metal alloys of manganese occurring in the equiatomic region,[1-4] we present here some considerations on the magnetic properties of the tetragonal PtMn phase with the CuAuI type crystal structure. Special interest in this phase arose from our previous findings regarding the sizes of the magnetic moments and their ordering in relation to composition and the interatomic distances in this crystal structure.[1,4]

Neutron diffraction investigations [4] of the three alloys $Pt_{45}Mn_{55}$, $Pt_{50}Mn_{50}$, and $Pt_{55}Mn_{45}$ showed antiferromagnetic arrangements of the magnetic moments with spin quantum numbers $2S_{Mn} = 4.0 \pm 0.2$ and $2S_{Pt} \approx 0$ (*i.e.* $2S_{Pt} < 0.2$). The moments of nearest-neighbour Mn atoms in (001) planes are antiparallel to each other, and the direction of the moments changes from parallel to c in the alloys $Pt_{45}Mn_{55}$ and $Pt_{50}Mn_{50}$ to perpendicular to c in $Pt_{55}Mn_{45}$.*

* Cooperative magnetic phenomena also occur in the ordered alloys Pt_3Mn and $PtMn_3$ with Cu_3Au type structure.[5-7] Pt_3Mn is ferromagnetic with $2S_{Mn} = 3.60 \pm 0.09$ and $2S_{Pt} = 0.17 \pm 0.04$, whereas neither the type of magnetic ordering nor the values of S_{Mn} and S_{Pt} are known for $PtMn_3$.

On substituting Mn for Pt atoms in the Pt layers, a decrease in the spin quantum number of Mn is expected due to the replacement of the interlayer Mn—Pt contacts by Mn—Mn contacts at a distance of less than 2.72 Å. Evidence for such decrease of S_{Mn} was not found for the alloy $Pt_{45}Mn_{55}$ where the 10 % substitution within the Pt layers is expected to change $2S_{Mn}$ from 4.0 in $Pt_{50}Mn_{50}$ to 3.8 in $Pt_{45}Mn_{55}$. (The uncertainty in the determination of $2S_{Mn}$ was $\pm$ 0.2.)

The range of homogeneity of the PtMn phase extends to $\sim$ 32 atomic % Pt on the Mn-rich side [1] and accordingly a check on this inconsistency was made by a neutron diffraction examination of the alloy $Pt_{35}Mn_{65}$ for which the reduction of S_{Mn} should be more pronounced.

EXPERIMENTAL

The alloy was prepared from 99.9 % pure Pt (Johnson, Matthey & Co., Ltd.) and 99.9 + % Mn (Johnson, Matthey & Co., Ltd., H_2 treated at 950°C for 5 h) by heating the mixed powders in evacuated, sealed silica tubes at 800°C for 5 days. After regrinding, the alloy was annealed at 950°C for another 5 days and quenched in water. (After the first set of experimental data had been collected, the alloy was reannealed at 600°C for 1 day, cooled slowly to 400°C and kept at this temperature for 7 days and finally cooled slowly to room temperature over a period of 14 days when further experiments were performed. Distinction between the two heat treatments proved unnecessary since the differences between the two sets of data were insignificant.)

X-Ray and neutron diffraction, and magnetic susceptibility measurements were carried out as described in the preceding paper.[4]

RESULTS AND DISCUSSION

The composition of the alloy was estimated to be 35.4 atomic % Pt on the basis of the tetragonal lattice dimensions $a_{chem} = 2.780 \pm 0.003$ Å, $c_{chem} = 3.761 \pm 0.001$ Å, using the *a* and *c versus* composition relationships found by Brun *et al.*[1] for this estimation. (The lattice dimensions are calculated from the X-ray powder diffraction data by applying the method of least squares. The indicated error limits correspond to twice the standard deviation obtained in these calculations.)

According to the present X-ray and neutron diffraction data the atomic arrangement of the alloy $Pt_{35}Mn_{65}$ consists of layers ($\perp c$) of Mn atoms alternating with partially substituted Pt layers, containing 70 % Pt and 30 % Mn distributed at random. Incomplete primary CuAuI type ordering resulting from mixing on the Mn sublattice is less than 3 % (estimated from the intensity data in Table 1). Failure to observe additional superstructure reflections (Table 1) confirms complete secondary intralayer disorder within the substituted layers.

The neutron diffraction patterns were in accordance with our previous findings [4] indexed in terms of a *C*-centred cell with $a = \sqrt{2}\, a_{chem} = 3.932 \pm 0.004$ Å, $c = c_{chem} = 3.761 \pm 0.001$ Å. Reflections with $H + K = 2n$ are nuclear reflections and those with $H + K = 2n + 1$ are magnetic reflections. The magnetic structure is of orthorhombic or lower symmetry (our calculations refer to Schubnikov group P_Cman) with the moments coupled and aligned

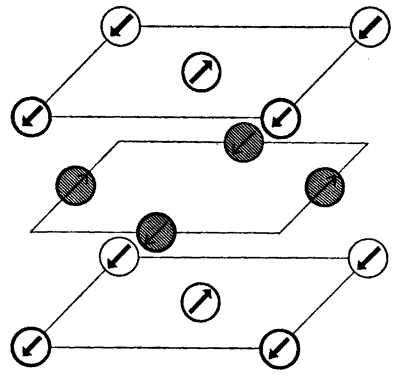

Fig. 1. Model showing the magnetic structure of $Pt_{35}Mn_{65}$. Open circles represent Mn atoms and shaded circles represent Pt, *viz.* Pt substituted by Mn atoms. The directions of the moments (indicated by arrows) within the (001) planes are undetermined.

antiferromagnetically within (001) planes. The moments of all the magnetic Mn atoms are ordered antiferromagnetically, *i.e.* the atoms in the complete Mn layers as well as the Mn atoms in the Pt layers, whereas the Pt atoms were found to be nonmagnetic. A model of the arrangement of the moments is shown in Fig. 1. The spin quantum numbers $2S_{Mn} = 3.1 \pm 0.2$ and $2S_{Pt} \approx 0$ ($2S_{Pt} < 0.2$) gave the best fit in the comparison of jF_o^2 and jF_c^2 (Table 1).

Table 1. Observed and calculated neutron diffraction data for $Pt_{35}Mn_{65}$ (at room temperature).

HKL	Type	jF_o^2	jF_c^2
100	Magn.	5.7	6.11
001	Nucl.	7.0	6.88
110	Nucl.	14.0	13.76
101	Magn.	6.8	6.63
111	Nucl.	1.3	1.21
200	Nucl.	0	0.68
002	Nucl.		0.34
210	Magn.	29.1	1.25
201	Nucl.		27.52
102	Magn.	3.4	3.18
211	Magn.	3.4	3.60
112	Nucl.	27.6	27.52

The reciprocal magnetic susceptibility *versus* temperature curve of $Pt_{35}Mn_{65}$ is shown in Fig. 2. The essential features of this curve correspond to those of other alloys of the PtMn phase reported by Brun *et al.*[1] and Andresen *et al.*[4] The weak ferromagnetism observed below $T_C \sim 250$°K is believed to result from a slight canting of the moments; *cf.* Andresen *et al.*[4] Other characteristic data extracted from the thermomagnetic curve (Fig. 2) are $T_N \sim 710$°K, $-\theta$ = large, μ_P = large, $\chi_{T_N} = 7.6_9 \times 10^{-6}$ e.m.u./g, and $\chi_0 \simeq 5.9 \times 10^{-6}$ e.m.u./g (extrapolated to 0°K).

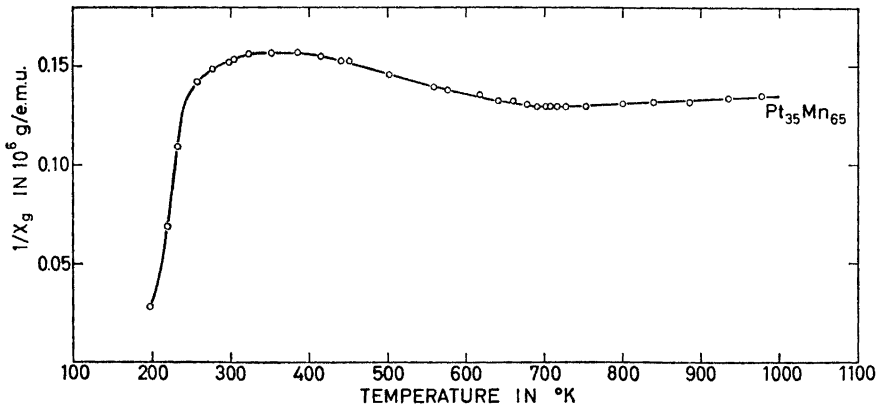

Fig. 2. Reciprocal magnetic susceptibility of $Pt_{35}Mn_{65}$ as a function of temperature.

The description of the magnetic exchange interaction in the PtMn phase by a Heisenberg Hamiltonian of the type

$$\mathcal{H} = -2J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

(counting only the antiferromagnetic exchange coupling between the nearest-neighbour Mn atoms) was found to give a reasonably selfconsistent picture of the observed magnetic properties of $Pt_{45}Mn_{55}$ and $Pt_{50}Mn_{50}$.[4] It therefore seemed of interest to use the data collected for the $Pt_{35}Mn_{65}$ alloy to obtain a new test of the applicability of the theory. With the observed values of χ_v = volume susceptibility at 0°K = 6.5×10^{-5} e.m.u./cm^3, N = number of Mn atoms per unit volume = 4.45×10^{22} Mn atoms/cm^3, and $S = S_{Mn} = 3.1/2$ and J = exchange parameter, g = Landé factor = 2, μ_B = Bohr magneton = 9.27×10^{-21} erg/gauss, k = Boltzmann constant = 1.380×10^{-16} erg/°K, and z = number of nearest Mn atoms, the combination of the formulae

$$\chi_v = Ng^2\mu_B{}^2/6zJ$$

$$T_N = 2zJS(S + 1)/3k$$

(obtained from the Weiss molecular field theory, *cf.* Kittel [8]) gives a calculated T_N value of 735°K. The calculated value compares quite well with the observed value $T_N \sim 710$°K showing that the data for $Pt_{35}Mn_{65}$ are selfconsistent when expressed in terms of this model.

The observed spin quantum numbers $2S_{Mn} = 3.1 \pm 0.2$ and $2S_{Pt} < 0.2$ in $Pt_{35}Mn_{65}$ are essentially consistent with the values $2S_{Mn} = 3.4$ and $2S_{Pt} = 0$ predicted on the basis of the simple model proposed in our previous paper [4] (see also Goodenough [9]). The assumptions being:

(i) An average of about one s electron per atom of the structure, with a d^{10} configuration on the Pt atoms and a d^5 configuration on the Mn atoms.

(ii) One electron in a d_{xy} bonding band directed towards Mn ligands (at a distance 2.780 Å) in the (001) plane, giving zero moment, but coupling the moments antiferromagnetically in (001).

(iii) One electron each in e_g orbitals $d_{x^2-y^2}$ and d_{z^2} which are localized (Mn—Mn distances of 3.932 Å along [100] and [010], and 3.761 Å along [001] of the magnetic unit cell).

(iv) One electron each in d_{yz} and d_{zx} which are spin parallel because of the internal molecular field on the Mn atoms resulting from the e_g electrons. d_{yz} and d_{zx} are directed towards neighbouring Pt (Mn) atoms (at a distance of 2.720 Å). In $Pt_{35}Mn_{65}$, where 30 % of the interlayer Mn—Pt contacts are replaced by Mn—Mn contacts, $2S_{Mn}$ should be reduced by $2 \times 0.3 = 0.6$, *i.e.* from 4.0 to 3.4. The 0.6 electrons per Mn atom form bonds which contribute zero moment.

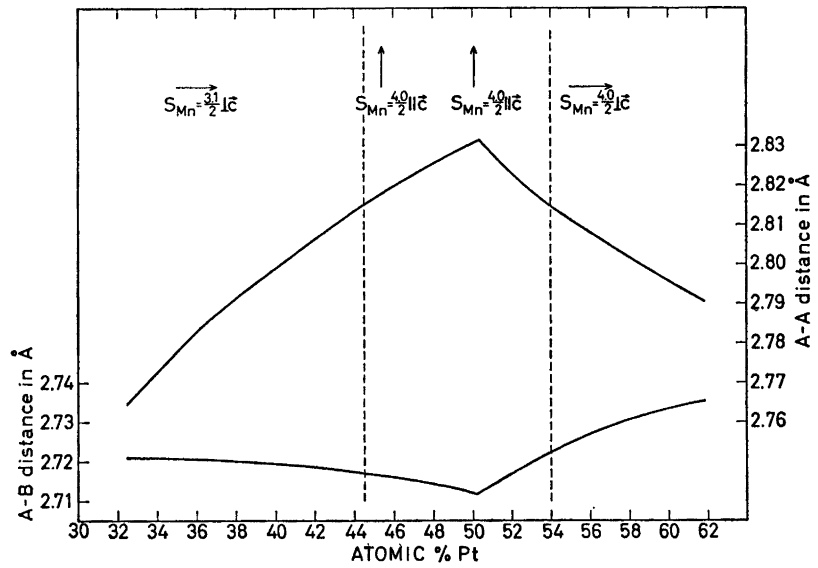

Fig. 3. Direction of Mn moments as a function of composition for the PtMn phase. Shortest interatomic distances A—A and A—B *versus* composition are also indicated. (In terms of the chemical (primitive CuAuI) unit cell A lies, *e.g.*, in 0,0,0 and B in $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.)

Another unexpected, but interesting observation of the present study s the direction ($\perp c$) of the moments in $Pt_{35}Mn_{65}$. As seen from Fig. 3 at least two shifts in the direction of the moments are found for the PtMn phase as a function of composition. It is furthermore interesting to notice (Fig. 3) that there is a correlation between the direction of the moments and the shortest Mn—Mn distance within the (001) planes. At a tentative, critical Mn—Mn distance of about 2.815 Å within the (001) planes the moments change direction from $\perp c$ to $\parallel c$.

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