Magnetic and Transport Properties of Frustrated \( \gamma \)-MnPd alloys

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Abstract. We have synthesized \( \gamma \)-Mn\(_{1-x}\)Pd\(_x\) alloys with \( x = 0.22 \) and 0.24 and carried out the susceptibility and resistivity measurements. The \( \gamma \)-Mn\(_{1-x}\)Pd\(_x\) shows the Néel transition to the non-coplanar antiferromagnetic 3Q phase at \( \sim \) 290 K for \( x = 0.22 \) and at \( \sim \) 250 K for \( x = 0.24 \). Below the Néel temperature, two characteristic temperatures, which support the existence of the magnetic and structural phase transitions, were observed. These results were used to construct a phase diagram of the \( \gamma \)-Mn\(_{1-x}\)Pd\(_x\) alloys with high \( x \) concentrations where non-collinear and/or non-coplanar spin structures are expected.

1. Introduction

Geometrically frustrated magnets have attracted much interest because of the possible emergence of novel magnetic phases. Competing magnetic interactions imposed by the geometrical arrangement of magnetic moments suppress the formation of a conventional magnetic order [1–3]. The concept of geometrical frustration is often discussed by treating an antiferromagnet consisting of a two-dimensional triangular lattice of Ising spins. In this case, the disordered spin state is associated with a macroscopic degeneracy in the ground state of the spin arrangements. On the other hand, in the XY-type or Heisenberg-type spin systems, non-collinear or non-coplanar spin arrangements are expected in order to minimize the energy. Recently, an increasing interest has been devoted to studying the properties of non-collinear and non-coplanar spin configurations in geometrically frustrated magnets because the associated vector and/or scalar spin chirality may induce exotic phenomena such as multiferroicity [4], unconventional anomalous Hall transport [5–8] and chiral spin liquid states [5,9]. Especially, non-collinear and non-coplanar antiferromagnets have been intensively investigated because of zero or vanishingly small magnetization [8,10–13].

Mn-based alloys generally have antiferromagnetic interaction due to the occupation of 3d orbitals [14]. Mn-based alloys consisting of the face-centered-cubic (fcc) lattice, which is one of three dimensional geometrically frustrated lattices, are considered to have various spin structures depending on the synthesis condition [15]. Here, we focus on \( \gamma \)-Mn disordered alloys, which are known to have complex magnetic and crystal structures including non-collinear and non-coplanar antiferromagnetic spin arrangements. The magnetic and crystal structures of \( \gamma \)-Mn...
alloys have been investigated by neutron scattering, X-ray diffraction, Mössbauer, susceptibility, Young’s modulus measurements and theoretical calculations [14, 16–24]. These experimental and theoretical studies for γ-Mn alloys found that the 1Q (collinear), 2Q (non-collinear), 2Q’ (non-collinear) or 3Q (non-coplanar) spin structures basically become stable in the case of \( a = b > c \) (face-centered-tetragonal : fct), \( a = b < c \) (fct), \( a > b > c \) (face-centered-orthorhombic : fco) or \( a = b = c \) (fcc), respectively [16, 17, 19, 23, 25] (Fig. 1). As the results of the previous measurements, the lattice distortions seemed to be connected with the spin structures. However, recent detailed investigations of γ-Mn alloys revealed that the distortions are not always accompanied by the magnetic phase transition. For instance, γ-MnNi alloys show that the fct-fcc structural transition is not accompanied by the 2Q-3Q magnetic transition and exhibits another type of magnetic structure 3Q’ (54.7° < θ < 90°), which has spins tilted along the ab-plane from the 3Q (θ = 54.7°) spin structure, in the concentration range of \( a = b < c \) (fct) [25]. It is expected that a new kind of spin structures induced by geometrical frustration such as the 3Q’ spin structure appears in other γ-Mn alloys. To understand the essence of the physics of non-collinear and non-coplanar antiferromagnetic spin textures, it is significant to investigate the magnetic and crystal structures in γ-Mn disordered alloys.

Hori et al. have studied the magnetic and crystal structures of γ-Mn\(_{1-x}\)Pd\(_x\) alloys (0.08 ≤ \( x \) ≤ 0.17), which have a platinum group metal similarly to γ-MnNi alloys, by X-ray diffraction, neutron scattering and susceptibility measurements [22]. However, there are few results of the fcc phase with \( x > 0.15 \) where the non-collinear 2Q and/or non-coplanar 3Q spin structures may appear. In this paper, we have investigated the magnetic and transport properties for γ-Mn\(_{1-x}\)Pd\(_x\) disordered alloys with high \( x \) concentrations.

2. Experimental

Polycrystalline samples of γ-Mn\(_{1-x}\)Pd\(_x\) alloys were prepared by melting mixtures of Mn (4N) and Pd (4N) using a mono-arc furnace filled with Ar gas at 1 atm. Before the melting, the surface oxides on Mn flakes were removed by etching with 5% nitric acid solution. Single crystals of the γ-Mn\(_{1-x}\)Pd\(_x\) were grown by the Czochralski method using a tetra-arc furnace (TAC-5100, GES) filled with Ar gas at 1 atm. The polycrystalline samples were used as starting materials. From powder X-ray diffraction measurements using a X-ray diffractometer (RINT-2100, Rigaku), the polycrystals and single crystals were confirmed to be the single phase. A scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis determined that the Pd concentrations of the samples are \( x = 0.22 \) and 0.24. The estimated error of our SEM-EDX analysis is within ±0.5 at.% Pd. The magnetic susceptibility was measured between 50 and 350 K under both zero-field-cooled (ZFC) and field-cooled (FC) conditions using a commercial SQUID magnetometer (MPMS, Quantum Design). The electrical resistivity was
3. Results and discussion

Results of magnetic and resistivity measurements for the $\gamma$-Mn$_{1-x}$Pd$_x$ alloys with $x$ = 0.22 and 0.24 are shown in Fig. 2(a) and 2(b), respectively. The temperature dependence of the susceptibility exhibits a kink at $\sim$ 290 K for $x$ = 0.22 and at $\sim$ 250 K for $x$ = 0.24. Similar kink was observed in the previous study for $\gamma$-MnPd and other $\gamma$-Mn alloys [14,19,22,23,25]. Neutron scattering and Young’s modulus measurements confirmed that this kink is related to the Néel transition [14,19,22,24]. Therefore, the Néel temperature $T_N$ of the $\gamma$-Mn$_{1-x}$Pd$_x$ alloys is determined by the kink in the susceptibility at $\sim$ 290 K for $x$ = 0.22 and at $\sim$ 250 K for $x$ = 0.24. Below $T_N$, the non-coplanar 3Q spin structure should be realized as observed in other $\gamma$-Mn alloys [14,16,17,23,25].

Furthermore, far below $T_N$, another kink in the susceptibility was observed at $\sim$ 110 K for $x$ = 0.22 and at $\sim$ 130 K for $x$ = 0.24, similarly observed in $\gamma$-MnNi and $\gamma$-MnIr alloys.
Fishman et al. pointed out that the magnetic phase transition from one Q-phase to another Q-phase can be marked by a small jump in the susceptibility of γ-Mn alloys [16]. Susceptibility, neutron scattering measurements and theoretical calculations for γ-MnNi alloys have revealed that the kink, which lies well below $T_N$, is ascribed to the 2Q-3Q(3Q') magnetic phase transition [25]. These results suggest that the magnetic phase transition between two different magnetic phases occurred at a characteristic temperature $T_1$, which is defined by the kink in the susceptibility observed at $\sim 110$ K for $x = 0.22$ and at $\sim 130$ K for $x = 0.24$ in the $\gamma$-Mn$_{1-x}$Pd$_x$ alloys. The hysteresis between the ZFC and FC susceptibility was also seen just below $T_1$. There are several possible origins for this hysteresis, which include spin glass freezing, spin canting or weak ferromagnetic moments arisen from the non-collinear or non-coplanar antiferromagnetic domain wall. To determine the origin of this hysteresis, more detailed measurements such as the AC and DC susceptibility measurements under various magnetic fields are needed.

The temperature dependence of the resistivity of the $\gamma$-Mn$_{1-x}$Pd$_x$ alloys shows metallic behavior, similarly observed in the previous study for $\gamma$-MnPd alloys [24]. The temperature derivative of the resistivity $d\rho/dT$ exhibits an obvious peak at $\sim 250$ K for $x = 0.22$ and at $\sim 220$ K for $x = 0.24$. According to the investigations for $\gamma$-MnNi and $\gamma$-MnPd alloys, two anomalies which have different origins can be observed in the resistivity measurements [24,25]. One is an anomaly derived from the Néel transition. The other is an anomaly originating from the fct-fcc structural phase transition well below $T_N$ [25]. Since the peak temperature $T_2$ observed in $d\rho/dT$ is $\sim 40$ K ($x = 0.22$) or $\sim 30$ K ($x = 0.24$) lower than $T_N$, the peak would not be derived from the Néel transition. However, it is also difficult to conclude that the fct-fcc phase transition occurs at $T_2$ from our results and the previous study [22]. As another possibility, the other magnetic and/or structural phase transitions can be assumed. However, to confirm the detailed phase, further experiments with a microscopic probe are necessary, such as X-ray and neutron diffraction measurements.

As a result of the susceptibility and resistivity measurements in the $\gamma$-Mn$_{1-x}$Pd$_x$ disordered alloys with high $x$ concentrations, three characteristic temperatures, $T_1$, $T_2$ and $T_N$ were obtained. Here, we added these characteristic temperatures in the magnetic and structural phase diagram given by Hori et al. [22], which is presented in Fig. 3.

**Figure 3.** Magnetic and structural phase diagram of the $\gamma$-Mn$_{1-x}$Pd$_x$ disordered alloys, together with the previous study [22] (black circles). The purple diamonds represent the characteristic temperature $T_1$ determined by the low-temperature kink in the susceptibility. The light blue triangles represent the characteristic temperature $T_2$ determined by the anomaly in the resistivity. The red squares represent the Néel temperature $T_N$.  

\[ T_1 = \text{characteristic temperature} \]

\[ T_2 = \text{characteristic temperature} \]

\[ T_N = \text{Néel temperature} \]
4. Summary
We have synthesized $\gamma$-Mn$_{1-x}$Pd$_x$ alloys with $x = 0.22$ and 0.24, and carried out the susceptibility and resistivity measurements. The susceptibility shows the Néel transition to the 3Q phase at $T_N \sim 290$ K for $x = 0.22$ and at $T_N \sim 250$ K for $x = 0.24$. Below $T_N$, moreover, the temperature derivative of the resistivity exhibits a peak at $\sim 250$ K for $x = 0.22$ and at $\sim 220$ K for $x = 0.24$, which is presumably ascribed to the magnetic and/or structural phase transition. In addition, the low-temperature susceptibility suggests that the magnetic phase transition occurred at $\sim 110$ K for $x = 0.22$ and at $\sim 130$ K for $x = 0.24$. To investigate the detailed low-temperature magnetic and crystal structures of the $\gamma$-Mn$_{1-x}$Pd$_x$ alloys with high $x$ concentrations, further experiments with a microscopic probe are needed.

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