Mn(Pt_{1-x}Pd_x)P: Isovalent Tuning of Mn Sublattice Magnetic Order

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Abstract

We report the growth and characterization of MnPd_xP, a rare-earth-free ferromagnet, with T_C ≈ 295 K and planar anisotropy, and conduct a substitutional study with its antiferromagnetic analogue MnPt_xP. We provide a solution route to grow large single crystals of MnPd_xP and the series Mn(Pt_{1-x}Pd_x)_5P by adding Mn into Pd-P and (Pt_{1-x}Pd_x)-P based melts. All compounds in the family adopt the layered anti-CeCoIn_5 type structure with the space group P4/mmm, and EDS and X-ray diffraction results indicate that MnPt_xP and MnPd_xP form a complete solid solution. Based on measurements of the temperature- and field-dependent magnetization and resistance, we construct a temperature-composition (T-x) phase diagram for Mn(Pt_{1-x}Pd_x)_5P and demonstrate that the initial antiferromagnetic order found in MnPt_xP is extraordinarily sensitive to Pd substitution. At low Pd fractions (x < 0.010), the single antiferromagnetic transition in pure MnPt_xP splits into a higher temperature ferromagnetic transition followed first, upon cooling, by a lower temperature ferromagnetic to antiferromagnetic transition and then by a re-entrant antiferromagnetic to ferromagnetic transition at even lower temperatures. The antiferromagnetic region makes up a bubble phase that persists up to x ≈ 0.008–0.009 for T ≈ 150 K, with all samples x < 0.008 recovering their initial ferromagnetic state upon further cooling to base temperature. Over the same low substitution range we find a non-monotonic change in the room temperature value of the unit cell volume, further suggesting that pure MnPt_xP is very close to an instability. Once x > 0.010, Mn(Pt_{1-x}Pd_x)_5P undergoes a only single transition into the ferromagnetic phase. The Curie temperature initially increases rapidly with x, rising from T_C ≈ 197 K at x = 0.013 to a maximum of T_C ≈ 312 K for x ≈ 0.62, and then falling back to T_C ≈ 295 K for pure MnPd_xP (x = 1.00). Given that Pt and Pd are isoelectronic, this work raises questions as to the origin of the extreme sensitivity of the magnetic ground state in MnPt_xP upon introducing Pd.

1 Introduction

Targeted design of tunable magnetic materials is active and key challenge for the materials chemistry and physics community. Achieving this goal necessitates understanding, at a microscopic level, what chemical and structural features underpin the magnetic properties of a given material. Whereas in magnetic semiconductors and insulators, theories based upon super-exchange interactions can often provide a satisfactory explanation of the magnetism in metallic compounds, it is far more challenging from a theoretical perspective to understand and therefore to predict whether a structure containing transition metals will be paramagnetic, ferromagnetic, or antiferromagnetic. This difficulty is particularly pronounced in the case of low-dimensional and/or itinerant magnetic metals, which show completely different electronic and magnetic properties from magnetic semiconductors. With these challenges in mind, detailed studies on isostructural or chemically similar intermetallic compounds with disparate magnetic properties may yield valuable insight into the physical parameters that ultimately determine the magnetism and hopefully provide guidelines for more targeted design of magnetic materials.

Based on our previous experimental work, magnetically active 3d metals (most frequently Cr, Mn, Fe, Co and Ni) occupying voids in complex intermetallic frame-
works can give rise to lower-dimensional structures of these magnetic metals. A prominent example is the $M(Pt, Pd)_5X$ family, where $M = Mn$, Fe and $X = P$, As, Se. These compounds all crystalize in the layered CeCoIn$_5$-type tetragonal structure with the space group $P4/mmm$ (#123). Despite sharing the same crystal structure, the magnetic properties of the $M(Pt, Pd)_5X$ materials are remarkably diverse. MnPt$_5$As is a $T_C \approx 280$ K ferromagnet, whereas the isovalent MnPt$_5$P orders antiferromagnetically below $T_N \approx 190$ K (likely with a small ferromagnetic, $q = 0$, component in addition to the predominantly antiferromagnetic order). FePt$_5$P is an itinerant antiferromagnet that undergoes three closely spaced transitions between $\approx 70$-90 K. Lastly, MnPd$_5$Se also shows antiferromagnetic order below $T_N \approx 80$ K, and a spin reorientation is observed upon further cooling below 50 K. The range of properties exhibited by the $M(Pt, Pd)_5X$ family suggests that the magnetism in these compounds is extremely sensitive to chemical composition, electron count, and steric considerations. The case of MnPt$_5$P is particularly interesting. As noted above, MnPt$_5$P orders antiferromagnetically, whereas MnPt$_5$As is a $\approx 280$ K ferromagnet. Very recently, exploratory solution growth of single crystal studies found that isovalent MnPd$_5$P also manifests ferromagnetic order near room temperature suggesting that both lattice expansion (towards MnPt$_5$As) and contraction (towards MnPd$_5$P) push the antiferromagnetic MnPt$_5$P toward a ferromagnetic ground state.

In this work, we present a substitutional study between MnPd$_5$P and MnPt$_5$P to better characterize the magnetism of the end members and to understand how the initially antiferromagnetic state of MnPt$_5$P evolves towards ferromagnetism in MnPd$_5$P. We successfully grew single and polycrystalline samples of MnPd$_5$P and Mn(Pt$_{1-x}$Pd$_x$)$_5$P using both solution growth and solid-state reaction techniques. Phase and structural analysis with X-ray diffraction and energy dispersive spectroscopy indicate that MnPd$_5$P and MnPd$_5$P form a full solid solution of Mn(Pt$_{1-x}$Pd$_x$)$_5$P. Magnetization measurements show that the essentially antiferromagnetic state in pure MnPt$_5$P is extraordinarily sensitive to Pd substitution. At Pd concentrations as low as $x < 0.01$, the pure antiferromagnetic transition found for pure MnPt$_5$P splits into a higher temperature ferromagnetic transition followed first, upon cooling, by a lower temperature ferromagnetic to antiferromagnetic transition and then by a re-entry into the ferromagnetic state at lower temperatures. The antiferromagnetic region makes up a bubble phase that persists up to $x \approx 0.008$ for $T \approx 150$ K, with all samples $x < 0.008$ recovering their initial ferromagnetic state upon further cooling to base temperature. Over the same low substitution range we find a possible non-monotonic change in the room temperature value of the $a$-lattice parameter and unit cell volume, further suggesting that pure MnPt$_5$P is very close to an instability. When $x > 0.010$, Mn(Pt$_{1-x}$Pd$_x$)$_5$P undergoes only a single, ferromagnetic, transition, where the Curie temperature initially increases with $x$ and is maximized at $\approx 312$ K for $x = 0.62$ Pd before decreasing to $\approx 295$ K in pure MnPd$_5$P. Considering that for $x > 0.01$, the rather gradual and non-monotonic $T_C$ variation does not track well with lattice parameters, or suggest particular sensitivity to Pd content, the fantastic sensitivity of the antiferromagnetic phase of Mn(Pt$_{1-x}$Pd$_x$)$_5$P for $x < 0.01$ is remarkable and suggests there is a qualitative change in the material that may well be associated with a change in the Fermi-surface topology, such as a Lifshitz transition. Qualitatively in-line with this proposal, electronic band structure calculations for MnPt$_5$P indeed show several pockets near the Fermi level which are significantly altered in MnPd$_5$P. Direct experiments to probe the electronic structure/density of states at the Fermi level are needed to further understand the extraordinary sensitivity of MnPt$_5$P to Pd alloying.

2 Experimental Details

2.1 Crystal Growth

We prepared and characterized both single crystalline and polycrystalline samples of MnPd$_5$P and Mn(Pt$_{1-x}$Pd$_x$)$_5$P. The Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals were grown from (Pt$_{1-x}$Pd$_x$)$_5$P based solutions as follows. Elemental Mn pieces (Puratronic, 99.98%), Pt powder (Engelhard, 99+ % purity), Pd powder (Engelhard, 99+ % purity), and red P pieces (Alpha-Aesar, 99.99%) were weighed according to nominal compositions of Mn$_5$Pt$_{71-x}$Pd$_x$P$_{20}$ (the actual compositions are given in Table 3 in the Appendix) and placed into the bottom of an alumina Canfield crucible set (CCS). The packed CCS were flame sealed into evacuated fused silica ampules that were backfilled with $\approx 1/6$ atm Ar gas. Using a box furnace, the ampules were slowly warmed to 250°C over 6 h and then to 1180°C over an additional 8 h. After dwelling at 1180°C for 6 h, the furnace was gradually cooled to 800°C (for samples with nominally less than 50% Pd) or to 830°C (for those with over 50% Pd) over $\approx 100$ h. Upon reaching the desired temperature, the excess liquid phase was decanted by inverting the ampules into a specially designed centrifuge with metal rotor and cups. After cooling to room temperature, the ampules were slowly warmed to 800°C over 6 h, and then to 1180°C over an additional 8 h. After dwelling at 1180°C for 6 h, the furnace was gradually cooled to 800°C (for samples with nominally less than 50% Pd) or to 830°C (for those with over 50% Pd) over $\approx 100$ h. Upon reaching the desired temperature, the excess liquid phase was decanted by inverting the ampules into a specially designed centrifuge with metal rotor and cups. After cooling to room temperature, the ampules and CCS were opened to reveal clusters of metallic plate-like crystals with typical dimensions of $\approx 3$ mm, and a representative picture of several crystals is shown in the inset to Figure 1.
and ground in Mn: Pt/Pd: P = 1:5:1 atomic ratio. The mixture was pressed into a pellet, and the pellet was placed into an alumina crucible and sealed in an evacuated silica tube. The sample tube was then heated to 1050°C at a rate of 40 °C per hour. After annealing for 2 days at 1050°C, the samples were slowly cooled down to room temperature at the speed of 10°C per hour. Both the single- and polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples were stable in moist air.

2.2 Phase and Structure Determination

Powder X-ray diffraction patterns were obtained using a Rigaku Miniflex-II instrument operating with Cu-Kα radiation with $\lambda = 1.5406 \text{ Å (Kα1)}$ and 1.5443 Å (Kα2) at 30 kV and 15 mA. The samples were prepared by grinding a representative number of crystals (5-10) to a fine powder. To determine the lattice parameters, the powder patterns were refined using the Rietveld method with GSAS-II software. To obtain better estimate of the uncertainty in the lattice parameters for samples very dilute in Pd, we collected and refined three separate patterns for samples with $x \leq 0.022$, and used the standard deviations of the refined values of $a$, $c$, and $V$ as error bars (see Figure 1b and 1c). For samples with $x > 0.022$, the fitting errors from the Rietveld refinements were used as the error bars.

Single crystal X-ray diffraction (SCXRD) experiments were conducted in a D8 Quest Eco diffractometer with Mo-Kα radiation ($\lambda = 0.71073 \text{ Å}$) equipped with Photon II detector. Empirically, we found that the solution grown single crystals of Mn(Pt$_{1-x}$Pd$_x$)$_5$P were not favorable for SCXRD, whereas very small single crystals picked from the sintered pellets (the solid-state reaction grown single crystals of Mn(Pt$_{1-x}$Pd$_x$)$_5$P) were more suitable and were used for the SCXRD. The samples were mounted on a Kapton loop and measured with an exposure time of 10 s per frame scanning 20 width of 0.5°. Structure refinement was performed in SHELXTL package using direct methods and full matrix least-squares on $F^2$ model. Anisotropic thermal parameters for all atoms were refined in SHELXTL. The VESTA software was used to plot the crystal structures.

2.3 Scanning Electron Microscopy (SEM) and Elemental Analysis

The Pd concentrations ($x$) in the Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals were determined by energy dispersive x-ray spectroscopy (EDS) quantitative chemical analysis using an EDS detector (Thermo NORAN Microanalysis System, model C10001) attached to a JEOL scanning-electron microscope (SEM). The compositions of each crystal were measured at several (3–6) different positions on the crystal’s face (perpendicular to the $c$-axis), revealing good homogeneity in each crystal. An acceleration voltage of 16 kV, working distance of 10 mm, and take off angle of 35° were used for measuring all standards and samples. A pure MnPt$_5$P single crystal ($x = 0.000$) was used as a standard for Mn, Pt, and P quantification, and a pure MnPd$_5$P single crystal ($x = 1.000$) was used as a standard for Pd. The spectra were fitted using NIST-DTSA II Microscopium software. The average compositions and error bars were obtained from these data, accounting for both inhomogeneity and goodness of fit of each spectra. Chemical compositions of the polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples were analyzed using a high vacuum Zeiss Sigma Field Emission SEM (FESEM) with Oxford INCA PentaFETx3 Energy-Dispersive Spectroscopy (EDS) system. Spectra were collected for 100 s from multiple areas of the crystals mounted on a carbon tape with an accelerating voltage of 20 keV.

2.4 Physical Property Measurements

For the single crystals, magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System (MPMS-classic) SQUID magnetometer operating in the DC measurement mode. The magnetic measurements were conducted with the field oriented parallel and perpendicular to the $c$-axis, where $c$ is axial direction relative to the plate-like crystals. For measurements with $H \perp c$, the samples were held in place between two plastic straws, and for $H \parallel c$, the samples were sandwiched from above and below between two plastic discs. A small pinhole was poked in the space between the discs to allow for evacuation. In the latter case, a blank background using the bare discs was first measured and the values subtracted.

The temperature dependent resistance of the Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals were measured on a Quantum Design Physical Property Measurement System (PPMS) operating in the AC transport mode with an applied current of 3 mA and frequency of 17 Hz. The samples were prepared by cutting the crystals into rectangular bars, and the contacts were made by spot welding 25 μm thick annealed Pt wire onto the samples in standard four point geometry. After spot welding, a small amount of silver epoxy was painted onto the contacts to ensure good mechanical strength, and typical contact resistances were $\approx 1 \Omega$.

2.5 Computational Details

Electronic band structure and density of states for MnPt$_5$P and MnPd$_5$P were calculated in density functional theory (DFT) using PBE[24] as the exchange-correlation functional with spin-orbit coupling (SOC) included. All DFT calculations were performed in the Vienna Ab initio Simulation Package (VASP) with a plane-wave basis set and projector augmented wave method[25]. The kinetic energy cutoff was 270 eV. We used a Γ-centered Monkhorst-Pack[26] (10×10×6) $k$-point
3 Results and Discussion

3.1 Phase, Composition, and Structural Analysis

We first analyzed our solution grown single crystals and sintered pellets with powder X-ray diffraction (PXRD) and energy dispersive spectroscopy (EDS) to determine the phase and assess the degree of Pd incorporation into the Mn(Pt<sub>1-x</sub>Pd<sub>x</sub>)<sub>5</sub>P alloys. Figure 1 shows the powder patterns collected for the ground, solution grown single crystals, and the EDS data is given in Table 3 in the Appendix. For all samples, the experimental PXRD patterns are in excellent agreement with the anticipated reflections for the P<sub>4</sub>/mmm structure of MnPt<sub>5</sub>P and MnPd<sub>5</sub>P. The EDS analysis likewise suggests a monotonic increase in the Pd incorporation into the 1-5-1 matrix as Pt is exchanged for Pd in the starting melts (see Figure 1).
The lattice parameters determined from Rietveld refinements of the powder patterns are shown in Figure 1b. The \( a \)-lattice parameter has a very shallow maximum at \( x = 0.054 \), but overall there is little change in \( a \) over the full compositional range. This is contrasted by the \( c \)-lattice parameter which decreases monotonically (nearly linearly) as the Pd fraction increases. Because \( a \) is nearly invariant with Pd doping, the unit cell volume \( V \), shown in Figure 1c, essentially mirrors the \( Pd \) dependence of \( c \), decreasing linearly as the Pd content is raised. The dashed green line in Figure 1c shows a linear fit between the volume of \( x = 0 \) and \( x = 1 \), and the experimental values closely follow the projected line, indicating that \( V \) follows Vegard’s law for a solid solution between MnPt\(_5\)P and MnPd\(_5\)P. At very low Pd fraction (\( x < 0.22 \)) the \( a \) lattice parameter and unit cell volume arguably each have a V-shape \( x \)-dependency, initially decreasing slightly before increasing again (see insets to Figure 1b and 1c). This non-monotonic is more evident in the volume, where a clear deviation from the Vegard’s law is observed for \( x < 0.22 \). We will return to this anomalous \( x \)-dependency at low substitution in the discussion of the magnetic properties.

To provide more detailed structural analysis of MnPd\(_5\)P and the Mn(Pt\(_{1-x}\)Pd\(_x\))\(_5\)P alloys, we conducted single crystal X-ray diffraction (SCXRD). The resulting crystallographic data, including atomic coordinates, site occupancies and equivalent isotropic thermal displacement parameters of MnPd\(_5\)P, are reported in Table 1 and Table 2 whereas crystallographic information on the Mn(Pt\(_{1-x}\)Pd\(_x\))\(_5\)P alloys are given in the Appendix in Tables 5 and 6. The results show that MnPd\(_5\)P and the Mn(Pt\(_{1-x}\)Pd\(_x\))\(_5\)P compounds crystalize in a tetragonal unit cell with the space group of \( P4/mmm \), like the previously reported MnPt\(_5\)P and MnPt\(_5\)As. The crystal structure is illustrated in Figures 2a and 2b and consists of layered motifs, with alternating layers of Mn@Pd\(_{12}\) face sharing polyhedra that span the \( ab \)-plane and which are separated by P layers along the \( c \)-axis. Consistent with the powder diffraction data, the single crystal XRD confirms that the Mn(Pt\(_{1-x}\)Pd\(_x\))\(_5\)P alloys maintain the parent lattice structure with the Pt and Pd atoms having mixed occupancy on the two atomic sites 1\( a \) and 4\( i \) as indicated in Figure 2b. Details on the Pt/Pd distributions on 1\( a \) and 4\( i \) sites for each phase are given in Table 6 in the Appendix. The SCXRD data may hint that the Pd atoms have a slight preference for occupying the 4\( i \) site over the 1\( a \) site; however, given the uncertainties in our refinements, this cannot be supported with confidence and our data indicates the Pt/Pd mixing is essentially a

| Atomic coordinates and equivalent isotropic displacement parameters of MnPd\(_5\)P at 300(2) K (\( U_{eq} \) is defined as one-third of the trace of the orthogonalized \( U_{ij} \) tensor (\( \text{Å}^2 \))) |
|---|
| Atoms | Wycoff | Occ. | \( x \) | \( y \) | \( z \) | \( U_{eq} \) (\( \text{Å}^2 \)) |
| Pd1 | 4\( i \) | 1 | 0 | 1/2 | 0.2948(1) | 0.015(1) |
| Pd2 | 1\( a \) | 1 | 0 | 0 | 0.012(2) |
| Mn3 | 1\( c \) | 1 | 1/2 | 1/2 | 0.022(2) |
| P4 | 1\( b \) | 1 | 0 | 0 | 1/2 | 0.016(2) |

Table 1: Single crystal structure refinement details for MnPd\(_5\)P at 300(2) K.

| | Refined Formula | MnPd\(_5\)P |
|---|---|---|
| F.W. (g/mol) | 617.91 |
| Space group: \( Z \) | \( P4/mmm \); 1 |
| \( a \) (\( \text{Å} \)) | 3.899 (2) |
| \( c \) (\( \text{Å} \)) | 6.867 (4) |
| \( V \) (\( \text{Å}^3 \)) | 104.42 (9) |
| \( \theta \) range (\( ^\circ \)) | 2.966-34.770 |
| No. reflections: \( R_{int} \) | 578; 0.0609 |
| No. independent reflections | 170 |
| No. parameters | 12 |
| \( R_1 \); \( wR_2 \) (\( I > 2d(I) \)) | 0.0509; 0.1204 |
| Goodness of fit | 1.282 |
| Diffraction peak and hole (e\(^-\)/\( \text{Å}^3 \)) | 2.656; -1.863 |

Table 2: Detailed structural analysis of MnPd\(_5\)P and the Mn(Pt\(_{1-x}\)Pd\(_x\))\(_5\)P alloys.
solid solution.

3.2 Magnetic and transport properties of Mn(Pt$_{1-x}$Pd$_x$)$_5$P

MnPt$_5$P enters into a spin-canted antiferromagnetic state at $T_N \approx 190$ K and preliminary data collected on MnPd$_5$P indicated that this material becomes ferromagnetic near room temperature. To understand how the magnetic state evolves as Pt is replaced with Pd, we conducted temperature and field dependent magnetization and transport measurements on our Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples, and the results are summarized in the temperature-composition ($T$-$x$) phase diagram given in Figure 3. The magnetization and transport data are outlined in Figures 4 and 5, and Figure 6 shows the field dependent magnetization isotherms collected at salient temperatures for $x < 0.010$ samples.

Temperature dependent magnetization ($M/H$) collected at $H = 1$ kOe with the field applied within the easy ab-plane ($H \perp c$) for the Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals is presented in Figure 4a, and Figure 4b shows $H = 50$ Oe data for $x < 0.010$ samples (See Figure 9 in the Appendix for the anisotropic $M(H)$ results). At low Pd substitution ($x < 0.010$), the initially narrow, antiferromagnetic-like, peak observed at 192 K for pure MnPt$_5$P substantially broadens as $x$ increases and forms a plateau-like maxima centered near $\approx 180$ K, whereas the weak upturn in $M/H$ below 100 K in MnPt$_5$P becomes a sharp increase reminiscent of ferromagnetic ordering. The ferromagnetic-like upturn moves to higher temperatures as $x$ increases, eventually merging with the initial higher temperature transition such that by $x = 0.008$, the $M/H$ data shows a very rapid increases at $\approx 193$ K followed by a second, subtle, increase beginning at $\approx 150$ K. Above $x > 0.010$, only a single ferromagnetic transition is observed, and the Curie temperature (determined more precisely from resistance measurements discussed below) increases with Pd alloying to a maximum at 312 K for $x = 0.62$ before falling gradually back to $\approx 295$ K for pure MnPd$_5$P.

To complement the temperature dependent $M/H$ data, we also measured the resistance of each sample from 1.8–375 K and present the data in Figure 5. The $R(T)$ results for low $x$ samples are given in Figure 5a and the derivatives $dR/dT$ used to assign the transition temperatures are shown in Figure 5b. Corresponding $R(T)$ and $dR/dT$ data for the $x > 0.03$ samples is shown in Figures 5c and 5d. As expected, all samples have metallic resistance that decreases with cooling, and the $R(T)$ datasets each show a clear kink followed by a rapid drop at the initial magnetic transition temperature $T_1$, characteristic of losing spin-disorder scattering as the samples enter a magnetically ordered state. The residual resistance ratios, $RRR = R(375 \text{ K})/R(1.8 \text{ K})$, are shown in the appendix in Figure 10 and are minimized at $x = 0.54$, consistent with the expectation for stronger scattering associated with the crystallographically disordered Pt and Pd atoms in the alloys.

At low Pd fraction, the samples with $0.0013 \leq x \leq 0.0053$ show a second transition $T_2$ just below the first, which is suppressed from $\approx 187$ K at $x = 0.0013$ to $\approx 177$ K at $x = 0.0053$. Further cooling reveals another lower temperature transition $T_3$ that increases with Pd alloy-
ing from $\approx 71$ K for $x = 0.00125$ to 160 K at $x = 0.009$. We note that the signature of $T_2$ is lost in the $x = 0.008$ and $x = 0.009$ resistance data, which is likely due to the close proximity of $T_2$ and $T_3$ at these compositions. This is consistent with the $M/H$ data (see Figure 4b), which shows the lower temperature ferromagnetic feature ($T_3$) essentially merging with the higher temperature transitions. $T_3$ is hysteretic between warming and cooling, implying it is first order (see Figure 10 in the Appendix for a close up view). The resistance curves for $0.033 \leq x \leq 1$ (Figure 5b) only show a single transition that increases rapidly with $x$ and is maximized at $\approx 312$ K before falling back to 295 K for pure MnPd$_5$P, consistent with the $M/H$ data in Figure 4.

Using the transitions identified in the temperature dependent $M/H$ and $R(T)$ data discussed above, we can identify the unique regions of the $T$–$x$ phase diagram shown in Figure 3. We find that the initial transition at 192 K in pure MnPt$_5$P splits into two transitions, $T_1$ and $T_2$, upon even minute, almost homeopathic, levels of Pd substitution. $T_1$ appears to be ferromagnetic and increases with $x$ to a maximum at 321 K for $x = 0.62$, whereas $T_2$ decreases gradually with $x$. The low-$x$ samples show a final third transition $T_3$ that increases with $x$ and intersects $T_2$ at approximately $x \approx 0.009$, such that $T_2$ and $T_3$ delineate a “bubble phase” on the phase diagram that extends out to $x \approx 0.009$. Below the bubble, the low-$x$ samples recover the original ferromagnetic state entered upon cooling through $T_1$.

To better determine the type of order found in each region of the phase diagram, Figure 6 presents magnetization isotherms measured at salient temperatures for the $x < 0.010$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples. (Figure 9 shows the $M(H)$ data for higher $x$ samples over a much higher applied field range.) As shown in Figure 6a, the $M(H)$

Figure 4: (a) Temperature dependence of $M/H$ for all Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals measured at $H = 1$ kOe. (b) Temperature dependence of $M/H$ for low $x$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P with $x < 1$ measured at $H = 50$ Oe.

Figure 5: (a) Temperature dependent resistance data for $0 \geq x \geq 0.022$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals with the data normalized to $R(375$ K). For clarity, the $R(T)$ curves are each offset by 0.1. (b) Derivatives of the datasets in (a). The peaks were used to determine transition temperatures and are marked with arrows. (c) and (d) are the respective $R(T)/R(375$ K) and $dR/dT$ data for $0.033 \geq x \geq 1$. 


Figure 6: Field-dependent magnetization isotherms measured at temperatures corresponding to different parts of the phase diagram for (a) \( x = 0 \), (b) \( x = 0.0013 \), (c) \( x = 0.0026 \), (d) \( x = 0.0053 \), (e) \( x = 0.008 \), (f) \( x = 0.009 \). Note that the x-axis scale for (a) and (b) extends to 10 kOe to observe the metamagnetic transitions.

curves for pure MnPt₅P show a series of metamagnetic transitions that shift to lower field as the temperature is lowered, indicating antiferromagnetic order. As outlined in our prior work, the magnetization curves for MnPt₅P all show a small saturation and measurable hysteresis at the lowest fields (under 0.2 kOe), implying that the antiferromagnetic order also has a small ferromagnetic (\( q = 0 \)) component (we use * in Figure 3b to denote the ferromagnetic component to the otherwise primarily antiferromagnetic state). Importantly, despite having a broad upturn in \( M/H \) below \( \approx 100 \) K (see Figures 4a and 4b), the 2 K \( M(H) \) isotherm for MnPt₅P is qualitatively the same as the higher temperature datasets, with a clear metamagnetic transition observed at \( \approx 1 \) kOe, indicating that MnPt₅P remains antiferromagnetic down to at least 2 K, which is consistent with the \( R(T) \) data for MnPt₅P showing only a single 192 K transition. This said, the very low metamagnetic field, that decreases with decreasing temperature, rather than the more standard increasing with decreasing temperature, strongly suggests a close energetic proximity to an ordered state with a larger ferromagnetic component.

Upon introduction of Pd, the \( M(H) \) isotherms measured above the “bubble” region of the phase diagram, at temperatures between \( T_1 \) and \( T_2 \), show a swift rise in \( M \) at low field followed by saturation at above \( \approx 1 \) kOe, implying that \( T_1 \) is a ferromagnetic transition (see 190 K data in Figures 6d–6f and 185 K data in Figure 6e). Within the bubble, between \( T_2 \) and \( T_3 \), the \( M(H) \) curves all show metamagnetic transitions that generally move to lower fields as the temperature is lowered (for a given value of \( x \)). Likewise, the \( M(H) \) datasets all show a small but measurable low-field saturation below \( \approx 0.2 \) kOe. Together, this information suggests that the bubble phase is the same spin-canted AFM* state found in pure MnPt₅P. Below \( T_3 \), the \( M(H) \) isotherms for Pd containing samples again are characteristic ferromagnetic behavior, with a rapid increase in \( M \) at low field followed by saturation at \( \approx 4.5 \ \mu_B/\text{f.u.} \). When the Pd fraction rises above \( x \approx 0.008-0.009 \), the \( M(H) \) isotherms show classic easy-plane ferromagnetic behavior at all temperatures below \( T_1 \) (see Figure 9 in the Appendix for \( M(H) \) data for \( x > 0.010 \)).

The \( M(H) \) data collected in the ferromagnetic phase (below \( T_1 \) for \( x < 0.010 \) and below \( T_3 \) for \( x > 0.010 \)) show very small (\( \approx 10-20 \) Oe), almost negligible, hysteresis on raising and lowering the field, implying that the ferromagnetism in Mn(Pt₁₋ₓPdₓ)₅P single crystals is very soft. Moreover, the \( M(H) \) results show that the Mn(Pt₁₋ₓPdₓ)₅P samples have relatively strong magnetic anisotropy where the \( ab \)-plane is the easy direction. Anisotropy fields \( H_A \) estimated by extrapolating the tangents of the \( H \perp c \) and \( H \parallel c \) datasets decrease monotonically as the Pd fraction rises (see Figure 8 in the Appendix), from \( \approx 108 \) kOe for \( x = 0.022 \) Pd to \( \approx 10 \) kOe in MnPd₅P, which likely reflects the decreasing
that MnPt₅P undergoes a transition, with very small Pd substitution, that manifests itself both in the lattice as well as the nature of the magnetic interactions. A clear candidate would be a Lifshitz type transition where the Fermi surface topology changes (i.e. small pockets appear/disappear) with small Pd substitution. Such an electronic transition can lead to changes in the density of states (DOS) at the Fermi energy as well as changes in the generalized electronic susceptibility, $\chi(q)$, which governs whether the magnetic order is anti- or ferromagnetic. To explore this possibility, we calculated electronic band structures for paramagnetic MnPt₅P and MnPd₅P.

The band structures are displayed in Figure 7, where the green shading represents the projection of Mn-3$d$ orbitals to the electronic states. As expected, the calculations indicate both MnPt₅P and MnPd₅P are metals, with multiple well dispersed bands crossing the Fermi energy ($E_F$). In both compounds, most of the bands near $E_F$ are composed of Mn-3$d$ based states. Most importantly, the band structure for pure MnPt₅P has several bands that graze, or come very close to $E_F$ at the $M$, $R$, and $A$ points in the Brillouin zone, as well as a Dirac-like set of bands along $X$–$M$. In MnPd₅P, the flat band sections near the $M$ and $R$ points move above $E_F$, and the band along the $X$–$M$ direction also moves up in energy. Furthermore, new flat band sections appear near $E_F$ in MnPd₅P along the $\Gamma$–$X$ and $A$–$Z$ directions. Admittedly, comparison of the end members MnPt₅P and MnPd₅P represents an extreme perturbation in reference to the $x \approx 0.02$ needed to stabilize purely ferromagnetic order in Mn(Pt$_{5-x}$Pd$_x$)$_5$P; however, the calculations do show that MnPt₅P has multiple pockets very near $E_F$ that are substantially changed in MnPd₅P, suggesting a Lifshitz transition is at least plausible in Mn(Pt$_{5-x}$Pd$_x$)$_5$P. Subsequent measurements that directly probe the electronic states at $E_F$, such as the thermopower and Hall effect, would be needed to explore and test this proposal.

3.3 Discussion

Our magnetic and transport measurements strongly suggest that the energy difference between ferromagnetic and antiferromagnetic states in MnPt₅P is exceptionally small, such that even the small perturbation of $x \approx 0.02$ Pd substitution on the Pt sites is sufficient to stabilize purely ferromagnetic order. At very low, essentially homeopathic levels of Pd $x < 0.01$, both antiferromagnetic and ferromagnetic phases are observed, and the antiferromagnetic state forms a bubble phase spanning pure MnPt₅P to $x \approx 0.008$–$0.009$. Whereas this magnetic phase diagram, shown in figure 3, describes the transitions below 200 K, non-monotonic changes in the $a$-lattice parameter and unit cell volume are also possibly detected at room temperature over essentially the same range of low $x$ (see Figure 1b and 1c). This suggests strength of spin orbit coupling accompanying substitution of the Pt with the smaller Z Pd.

4 Summary and Conclusions

We determined that ferromagnetic MnPd₅P adopts the anti-CeCoIn₅ structure with the space group $P4/mmm$ and conducted a detailed substitutional study with its isostructural antiferromagnetic analogue MnPt₅P. We demonstrate a solution route to grow large single crystals of both MnPd₅P and the alloys Mn(Pt$_{1-x}$Pd$_x$)$_5$P. EDS and X-ray diffraction data support the formation of a full Mn(Pt$_{1-x}$Pd$_x$)$_5$P solid solution that maintains the tetragonal anti-CeCoIn₅ structure. The magnetic data show that the primarily antiferromagnetic state in pure MnPt₅P is extremely sensitive to Pd substitution, and as little as $x > 0.010$ Pd stabilizes purely ferromagnetic order. At low $x < 0.010$, the single antiferromagnetic transition in MnPt₅P splits into a higher temperature ferromagnetic transition and lower temperature...
ferromagnetic-to-antiferromagnetic and lower temperature antiferromagnetic to ferromagnetic transition. The antiferromagnetic region forms a bubble-region in the $T$–$x$ phase diagram which persists up to $x \approx 0.008$–0.009, and further cooling recovers the original ferromagnetic state as the samples approach base temperature. Room temperature values of the $a$-lattice parameter and unit-cell-volume also manifest anomalous behavior for $x \approx 0.010$, suggesting that some electronic topological phase transition, such as a Lifshitz transition, may be responsible for the changes in both magnetic ordering as well as structural features. Electronic band structure calculations indicate pure MnPt$_5$P has several pockets close to the Fermi level that could be involved in such a transition. Beyond $x > 0.010$, the ferromagnetic Curie temperature is substantially enhanced with Pd incorporation to $\approx 312$ K at $x = 0.62$ before falling back to 295 K in pure MnPd$_5$P. All Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples have strong magnetic anisotropy in which the $ab$-plane is the easy direction, and the anisotropy field decreases from $\approx 108$ kOe for $x = 0.022$ Pd to $\approx 10$ kOe for MnPd$_5$P, likely a result of reduced spin orbit coupling.

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Conflicts of Interest

The authors have no conflicts of interest to declare.

6 Appendix

6.1 EDS analysis of Mn(Pt$_{1-x}$Pd$_x$)$_5$P

Table 3 lists the nominal compositions Mn$_9$Pt$_{71-y}$Pd$_y$P$_{20}$ used for the growth of Mn(Pt$_{1-x}$Pd$_x$)$_5$P single crystals and the corresponding values of $x$ determined by EDS from each batch. Note that starting compositions do not correspond to exact stoichiometry (i.e. $y \neq x$) because the intention for solution growth is to intersect the liquidus surface for crystalization of Mn(Pt$_{1-x}$Pd$_x$)$_5$P on cooling, not to be directly “on-line”. Table 3 gives the same information for the polycrystalline samples obtained from solid-state reactions. The values of $x$

| Nominal $y$ | Nominal $x$ | EDS $x$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P
|-------------|-------------|---------------------|
| 0.25        | 0.0035      | 0.0013 ± 0.0014     |
| 0.5         | 0.0070      | 0.003 ± 0.0014      |
| 1           | 0.014       | 0.0055 ± 0.0005     |
| 1.5         | 0.021       | 0.0082 ± 0.0007     |
| 1.75        | 0.025       | 0.009 ± 0.0001      |
| 2.25        | 0.032       | 0.013 ± 0.002       |
| 3           | 0.042       | 0.022 ± 0.001       |
| 6           | 0.0845      | 0.033 ± 0.003       |
| 9           | 0.13        | 0.0635 ± 0.003      |
| 16          | 0.225       | 0.116 ± 0.005       |
| 23          | 0.32        | 0.188 ± 0.005       |
| 47          | 0.66        | 0.543 ± 0.004       |
| 50          | 0.70        | 0.623 ± 0.004       |

Table 4: Chemical compositions determined from EDS analysis for the solution-grown single crystals of Mn(Pt$_{1-x}$Pd$_x$)$_5$P. The nominal compositions used for the growth were Mn$_9$Pt$_{71-y}$Pd$_y$P$_{20}$, and we also give the nominal Pd:Pt fraction ($x$) in each. The EDS values of $x$ represent the averages of 3-6 scans on each sample and the error bars were obtained considering both the EDS fitting errors and standard deviations of each measurement (see text).

| Nominal $x$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P | EDS $x$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P |
|-------------------------------------|----------------------------------|
| 0.2                                 | 0.188(5)                        |
| 0.4                                 | 0.39(2)                         |
| 0.5                                 | 0.502(5)                        |
| 0.6                                 | 0.589(3)                        |
| 0.8                                 | 0.81(1)                         |
Table 5: Single crystal structure refinement information for Mn(Pt$_{1-x}$Pd$_x$)$_2$P at 300(2) K. (The standard deviations are indicated by the values in parentheses). The single crystals used for data collection and refinement were picked from the sintered pellets.

| Loaded composition | Refined Formula | MnPd$_4$P | Mn(Pt$_{0.6}$Pd$_{0.8}$)$_2$P | Mn(Pt$_{0.6}$Pd$_{0.4}$)$_2$P | Mn(Pt$_{0.6}$Pd$_{0.5}$)$_2$P | Mn(Pt$_{0.6}$Pd$_{0.5}$)$_2$P | Mn(Pt$_{0.6}$Pd$_{0.4}$)$_2$P | Mn(Pt$_{0.6}$Pd$_{0.3}$)$_2$P |
|--------------------|-----------------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| R.F.W. (g/mol)     | 617.91          | 694.18    | 819.24          | 848.5           | 875.11          |
| Space group; Z     | P4/mmm; 1       | P4/mmm; 1 | P4/mmm; 1       | P4/mmm; 1       | P4/mmm; 1       |
| a (Å)              | 3.899(2)        | 3.894(1)  | 3.887(2)        | 3.888(2)        | 3.901(3)        |
| c (Å)              | 6.867(4)        | 6.855(1)  | 6.853(2)        | 6.861(2)        | 6.892(4)        |
| V (Å$^3$)          | 104.42(2)       | 103.93(2) | 103.54(4)       | 103.73(5)       | 104.93(11)      |
| θ range (°)        | 2.966-34.77     | 5.26-34.28 | 5.24-34.89      | 2.969-34.87     | 5.919-34.64     |
| No. reflections; R$_{int}$ | 578; 0.0699 | 1397; 0.0293 | 999; 0.0444 | 904; 0.0549 | 214; 0.0233 |
| No. independent reflections | 170 | 173 | 166 | 167 | 94 |
| No. parameters     | 12              | 14        | 14              | 14              | 14              |
| R$_{1}$: wR$_{2}$ (I > 2σ(I)) | 0.0509; 0.1204 | 0.0253; 0.0603 | 0.0429; 0.1026 | 0.0417; 0.1080 | 0.0373; 0.0947 |
| Goodness of fit    | 1.285           | 1.346     | 1.331           | 1.429           | 1.154           |
| Diffraction peak and hole (ε$^{-1}$/Å$^2$) | 2.656; -1.863 | 2.632; -1.926 | 7.771; -3.765 | 7.323; 5.219 | 2.579; -3.540 |
| Temperature (K)    | 300 (2)         | 299 (2)   | 301 (2)         | 300 (2)         | 301 (2)         |

Table 6: Atomic coordinates, occupancies and isotropic displacement parameters of Mn(Pt$_{1-x}$Pd$_x$)$_2$P at 300(2) K. ($U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor (Å$^2$)).

| Atom  | Wyckoff. | Occ. | x     | y     | z    | $U_{eq}$ |
|-------|----------|------|-------|-------|------|----------|
| MnPd$_4$P |        |      |       |       |      |          |
| Pd1   | 4i       | 1    | 0 1/2 | 0.2948 | 1    | 0.015(1) |
| Pd2   | 1a       | 1    | 0    | 0     | 0.012(2) |
| Mn3   | 1c       | 1    | 1/2  | 0     | 0.022(1) |
| P4    | 1b       | 1    | 0    | 0     | 0.016(2) |

| Mn(Pt$_{0.6}$Pd$_{0.8}$)$_2$P |        |      |       |       |      |          |
| Pd1   | 4i       | 0.84(2) | 0 1/2 | 0.29385(9) | 0.0058(2) |
| Pt2   | 4i       | 0.22(2) | 0 1/2 | 0.2948(1) | 0.0058(2) |
| Pd3   | 1a       | 0.78(2) | 0    | 0     | 0.0046(3) |
| Pt4   | 1a       | 0.22(2) | 0    | 0     | 0.0046(3) |
| Mn3   | 1c       | 1    | 1/2  | 0     | 0.0128(9) |
| P4    | 1b       | 1    | 0    | 0     | 0.0076(11) |

| Mn(Pt$_{0.4}$Pd$_{0.6}$)$_2$P |        |      |       |       |      |          |
| Pd1   | 4i       | 0.57(6) | 0 1/2 | 0.29296(17) | 0.0056(4) |
| Pt2   | 4i       | 0.43(6) | 0 1/2 | 0.29296(17) | 0.0056(4) |
| Pd3   | 1a       | 0.55(6) | 0    | 0     | 0.0037(6) |
| Pt4   | 1a       | 0.45(6) | 0    | 0     | 0.0037(6) |
| Mn3   | 1c       | 1    | 1/2  | 0     | 0.020(2) |
| P4    | 1b       | 1    | 0    | 0     | 0.006(2) |

| Mn(Pt$_{0.2}$Pd$_{0.8}$)$_2$P |        |      |       |       |      |          |
| Pd1   | 4i       | 0.50(8) | 0 1/2 | 0.29274(18) | 0.0078(5) |
| Pt2   | 4i       | 0.50(8) | 0 1/2 | 0.29274(18) | 0.0078(5) |
| Pd3   | 1a       | 0.42(6) | 0    | 0     | 0.0049(7) |
| Pt4   | 1a       | 0.58(6) | 0    | 0     | 0.0049(7) |
| Mn3   | 1c       | 1    | 1/2  | 0     | 0.015(3) |
| P4    | 1b       | 1    | 0    | 0     | 0.011(3) |

| Mn(Pt$_{0.4}$Pd$_{0.6}$)$_2$P |        |      |       |       |      |          |
| Pd1   | 4i       | 0.43(6) | 0 1/2 | 0.29254(11) | 0.0084(6) |
| Pt2   | 4i       | 0.57(6) | 0 1/2 | 0.29254(11) | 0.0084(6) |
| Pd3   | 1a       | 0.38(6) | 0    | 0     | 0.0068(7) |
| Pt4   | 1a       | 0.62(6) | 0    | 0     | 0.0068(7) |
| Mn3   | 1c       | 1    | 1/2  | 0     | 0.012(3) |
| P4    | 1b       | 1    | 0    | 0     | 0.014(4) |

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**Figure 8**: EDS values of $x$ Pd in Mn(Pt$_{1-x}$Pd$_x$)$_2$P compared to the nominal $x$ added to the starting crystal growth compositions. The inset shows a closeup of the low-$x$ data, and the dashed line is a linear fit to the data up to nominally $x = 0.0845$.

The Pd fraction is calculated as $f_{Pd} = x$, and $f_{Pt} = 1-x$. The EDS values of $x$ Pd were measured relative to the total amount of Pt and Pd detected in each sample. The fitting error was only used for $x = 0.0001$. We calculated $x$ relative to the total amount of Pt and Pd detected in each sample, i.e., $x = f_{Pd} / (f_{Pt} + f_{Pd})$, where $f_{Pt}$ and $f_{Pd}$ represent the quantity of Pt(Pd) found in each sample. For both the solution growth single crystals and polycrystalline samples, we observe a monotonic enrichment of the EDS Pd fraction as the starting growth compositions become richer in Pd. For the single crystalline sample with nominal $y = 0.25$ and EDS $x = 0.00013$, the Pd fraction is under the detection limit of our instrument (the fitting errors to the EDS spectra were $\approx 10$ times greater than the detected quantity of Pd). This is unsurprising given the extremely dilute
quantity added to the initially melt ($y = 0.25$, which is $\approx 0.35\%$ Pd relative to the total quantity of Pt and Pd); however, the significant differences in the magnetic and transport properties between this sample and those of pure MnPt₅P imply very small but finite Pd incorporation (see Figures 3-6 in the main text). Given the detected Pd in this sample is below the resolution of our instrument, to estimate the Pd fraction, we extrapolated the linear trend between nominal and EDS values of $x$ to nominally $x = 0.0035$ (see the inset to Figure 8), which gives an estimate of $x = 0.0013$ for the most dilute sample.

6.2 Crystallographic information for Mn(Pt₁₋ₓPdₓ)₅P

Table 5 gives the refinement information and statistics for the single crystal XRD refinements of Mn(Pt₁₋ₓPdₓ)₅P samples. The single crystals used for these measurements were picked from the single-crystalline pellets (solid-state reactions). The atomic positions and isotropic displacement parameters are listed in Table 6. The results indicate that MnPt₅P and the Mn(Pt₁₋ₓPdₓ)₅P compounds all adopt the layered tetragonal ($P4/mmm$) anti-CeCoIn₅ type structure. The single crystal XRD refinements support mixed occupancy between Pt and Pd on the two atomic sites $\text{1a}$ and $\text{4i}$, indicating the formation of a Mn(Pt₁₋ₓPdₓ)₅P solid solution. As shown in Table 6, the Pd atoms may have a slight preference for occupying the $\text{4i}$ site over the $\text{1a}$ site; however, given the uncertainties of our experiments we are not able to confidently assert a site preference for the Pt or Pd atoms.

6.3 Additional Data for Mn(Pt₁₋ₓPdₓ)₅P Single Crystals

Figure 9 shows the magnetization isotherms measured at 2 K for Mn(Pt₁₋ₓPdₓ)₅P where $0.022 \geq x \geq 1$. All datasets show field dependencies that are characteristic
of ferromagnetic order in which the $ab$-plane is the easy direction (i.e. $H \perp c$). The saturation magnetization are all on the order of 4-4.5 $\mu_B$/f.u., with $\approx 10\%$ variation amongst the samples, and there is no clear trend in the magnitude of $\mu_{sat}$ as a function of the Pd fraction. The discrepancies likely represent a combination of weighing errors, uncertainty in $x$, and intrinsic changes in $\mu_{sat}$ as $x$ changes. Ultimately, the primary conclusion drawn from Figure 9 is that $x > 0.01$ Mn(Pt$_{1-x}$Pd$_x$)$_5$P are unambiguously easy-plane ferromagnets below $T_1$.

Extrapolating the tangents of the $M(H)$ isotherms in Figure 9 to their intersection point gives an estimate of the anisotropy fields $H_A$, which are plotted explicitly in Figure 11. We find that $H_A$ decreases monotonically with increasing Pd fraction, strongly suggesting that the weakening magnetic anisotropy is governed by the decreasing strength of spin orbit coupling accompanying the replacement of Pt atoms with lower $Z$ Pd.

### 6.4 Magnetic Data for Polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P

Because the crystallographic data for MnPd$_5$P and Mn(Pt$_{1-x}$Pd$_x$)$_5$P was obtained from small single crystals picked from solid state reactions, we also measured the magnetic properties of the sintered pellets to ensure consistency with the solution-grown single crystals discussed in the main text. The magnetic properties of the polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P ($x = 0.2, 0.4, 0.5, 0.6, 0.8, \text{ and } 1$) were measured in a Quantum Design PPMS Dynacool (QD-PPMS) at the National High Magnetic Field Laboratory over a temperature range of 1.8 to 400 K with the applied field of 1 kOe. Additionally, magnetic measurements of Pt doped compounds were carried out in a vibrating sample magnetometer (VSM) in a Quantum Design PPMS system over a temperature range of...
The Magnetic data for the polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples is displayed in Figures 12 and 13. Like the single crystals discussed above, the Pd-containing polycrystalline samples, which have 0.2 $\leq x \leq$ 1, also show ferromagnetic behavior where $T_C$ is maximized near 312 K for $\approx x = 0.60$ Pd. However, in addition to the Mn(Pt$_{1-x}$Pd$_x$)$_5$P primary phase, the polycrystalline pellets also contained a small fraction of a ferromagnetic impurity, likely MnPt$_3$ ($T_C \approx 390$ K).

Owing to the strong response of ferromagnetism to an applied magnetic field, even small ferromagnetic impurities are easily detected in magnetization measurements, and our polycrystalline samples with $x < 0.5$ all show high temperature ($T > 300$ K) ferromagnetic-like transitions that are not observed in any of the datasets collected on the single crystals. An analogous MnPd$_5$ phase also exists, but orders antiferromagnetically, which likely explains why the polycrystalline Mn(Pt$_{1-x}$Pd$_x$)$_5$P samples with $x > 0.5$ do not show evidence for a second transition. As the ordering of MnPt$_3$ could easily be misinterpreted as a second, higher temperature, transition in the Pt-rich samples, the contrast between single and polycrystalline data is an excellent demonstration of the advantages of solution growth, which allows us to produce high quality Mn(Pt$_{1-x}$Pd$_x$)$_5$P crystals free of significant contamination by magnetic impurities. The field dependent magnetization isotherms for the polycrystalline samples are shown in Figure 13 and show soft ferromagnetic behavior below $T_1$ and saturated moments $\approx 4-4.5 \mu_B$/f.u. at 2 K. Excluding the transitions from the MnPt$_3$, the intrinsic Curie temperatures of the polycrystalline samples are otherwise in good agreement with those inferred from the data collected on single crystals.

References

(1) Dietl, T. A Ten-Year Perspective on Dilute Magnetic Semiconductors and Oxides. Nature Materials 2010, 9, 965–974.
(2) Goodenough, J. B. Direct Cation–Cation Interactions in Several Oxides. Physical Review 1960, 117, 1442.
(3) Samolyuk, G. D.; Miller, G. J. Relation Between Chemical Bonding and Exchange Coupling Approaches to the Description of Ordering in Itinerant Magnets. Journal of Computational Chemistry 2008, 29, 2177–2186.
(4) Fei, Z.; Huang, B.; Malinowski, P.; Wang, W.; Song, T.; Sanchez, J.; Yao, W.; Xiao, D.; Zhu, X.; May, A. F., et al. Two-Dimensional Itinerant Ferromagnetism in Atomically Thin Fe$_3$GeTe$_2$. Nature Materials 2018, 17, 778–782.
(5) Zhang, Y.; Miller, G. J.; Fokwa, B. P. Computational Design of Rare-Earth-Free Magnets with the Ti$_3$Co$_5$B$_2$-Type Structure. Chemistry of Materials 2017, 29, 2535–2541.
(6) Shankhari, P.; Scheifers, J. P.; Hermus, M.; Yubuta, K.; Fokwa, B. P. Unexpected Trend Deviation in Isoelectronic Transition Metal Borides $A_3T_5B_2$ ($A = \text{group 4, } T = \text{group 9}$): Ti$_3$Co$_5$B$_2$-vs. Perovskite-Type Studied by Experiments and DFT Calculations. Zeitschrift für anorganische und allgemeine Chemie 2017, 643, 1551–1556.
(7) Chen, B.; Yang, J.; Wang, H.; Imai, M.; Ohta, H.; Michioka, C.; Yoshimura, K.; Fang, M. Magnetic Properties of Layered Itinerant Electron Ferromagnet Fe$_3$GeTe$_2$. Journal of the Physical Society of Japan 2013, 82, 124711.
(8) Fokwa, B. P. T.; Lucken, H.; Dronskowski, R. Rational Design of Complex Borides – One-Electron-Step Evolution from Soft to Semi-Hard Itinerant Ferromagnets in the New Boride Series Ti$_2$FeRu$_5$–nRhnB$_2$ (1 $\leq n \leq$ 5). European Journal of Inorganic Chemistry 2011, 2011, 3926–3930.
Figure 13: Field dependent magnetization isotherms measured at 2 K on pellets of polycrystalline Mn(\(\text{Pt}_{1-x}\text{Pd}_x\))\(_5\)P.

(9) Gui, X.; Klein, R. A.; Brown, C. M.; Xie, W. Chemical Bonding Governs Complex Magnetism in MnPt\(_5\)P. *Inorganic Chemistry* 2020, 60, 87–96.

(10) Gui, X.; Marshall, M.; Dissanayaka Mudiyanse-lage, R. S.; Klein, R. A.; Chen, Q.; Zhang, Q.; Shelton, W.; Zhou, H.; Brown, C. M.; Cao, H.; Greenblatt, M.; Xie, W. Spin Reorientation in Antiferromagnetic Layered FePt\(_5\)P. *ACS Applied Electronic Materials*, 3.

(11) Gui, X.; Xie, W. Crystal structure, magnetism, and electronic properties of a rare-earth-free ferromagnet: MnPt\(_5\)As. *Chemistry of Materials* 2020, 32, 3922–3929.

(12) Dissanayaka Mudiyanse-lage, R. S.; Zhang, Q.; Marshall, M.; Croft, M.; Shu, Z.; Kong, T.; Xie, W. Spin Reorientation in Antiferromagnetic MnPd\(_5\)Se with an Anti-CeCoIn5 Structure Type. *Inorganic Chemistry* 2022, 61, 3981–3988.

(13) Slade, T. J.; Canfield, P. C. Use of Refractory-Volatile Element Deep Eutectic Regions to Grow Single Crystalline Intermetallic Compounds. *Zeitschrift für anorganische und allgemeine Chemie* 2022, 648, e202200145.

(14) Canfield, P. C.; Kong, T.; Kaluarachchi, U. S.; Jo, N. H. Use of Frit-Disc Crucibles for Routine and Exploratory Solution Growth of Single Crystalline Samples. *Philosophical Magazine* 2016, 96, 84–92.

(15) Canfield Crucible Sets, [https : // www. lspceramics.com/canfield-crucible-sets-2/](https://www.lspceramics.com/canfield-crucible-sets-2/). Accessed: 2022-03-23.

(16) Canfield, P. C. New Materials Physics. *Reports on Progress in Physics* 2019, 83, 016501.

(17) Toby, B. H.; Von Dreele, R. B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography* 2013, 46, 544–549.

(18) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallographica Section C: Structural Chemistry* 2015, 71, 3–8.

(19) Muller, P.; Herbst-Irmer, R.; Spek, A.; Schneider, T.; Sawaya, M., *Crystal Structure Refinement: A Crystallographer’s Guide to SHELXL*; OUP Oxford: 2006; Vol. 8.

(20) Momma, K.; Izumi, F. VESTA: a Three-Dimensional Visualization System for Electronic and Structural Analysis. *Journal of Applied crystallography* 2008, 41, 653–658.

(21) Newbury, D. E.; Ritchie, N. W. In *Scanning Microscopies*, 2014; Vol. 9236, pp 90–106.

(22) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Physical Review* 1964, 136, B864.

(23) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140, A1133–A1138.
(24) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. Phys. Rev. Lett. 2008, 100, 136406.

(25) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169–11186.

(26) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Computational Materials Science 1996, 6, 15–50.

(27) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 1994, 50, 17953–17979.

(28) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 1976, 13, 5188–5192.

(29) Fisher, M. E.; Langer, J. S. Resistive Anomalies at Magnetic Critical Points. Phys. Rev. Lett. 1968, 20, 665–668.

(30) Antonini, B.; Lucari, F.; Menzinger, F.; Paoletti, A. Magnetization Distribution in Ferromagnetic MnPt$_3$ by a Polarized-Neutron Investigation. Phys. Rev. 1969, 187, 611–618.

(31) Antonini, B.; Felici, M.; Menzinger, F. Spin waves and exchange interactions in MnPt$_3$ ferromagnetic alloy. Physics Letters A 1969, 30, 310–311.

(32) Sato, H.; Toth, R. Long-Period Superlattice Pd$_3$Mn II and Its Large Tetragonal Distortion. Phys. Rev. 1965, 139, A1581–A1593.

(33) Kre´n, E.; Ka´d´ar, G. Crystal and magnetic structures in the Mn-Pd system near MnPd$_3$. Physics Letters A 1969, 29, 340–341.

(34) Krén, E.; Kádár, G.; Márton, M. Neutron diffraction study of the MnPd$_3$ phase. Solid State Communications 1972, 10, 1195–1198.