High Temperature Ferromagnetism in Cr$_{1+x}$Pt$_{5-x}$P

Tyler J. Slade,$^{1,2}$*, Nao Furukawa,$^{1,2}$ Tanner R. Smith,$^{1,2}$ Juan Schmidt,$^{1,2}$ Ranuri S. Dissanayaka Mudiyanselage,$^{3}$ Lin-Lin Wang,$^1$ Weiwei Xie,$^{3,4}$ Sergey L. Bud’ko,$^{1,2}$ Paul C. Canfield$^{1,2}$

$^1$Ames National Laboratory, US DOE, Iowa State University, Ames, Iowa 50011, USA
$^2$Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
$^3$Department of Chemistry and Chemical Biology, The State University of New Jersey Rutgers, Piscataway, NJ 08854, USA
$^4$Department of Chemistry, Michigan State University, East Lansing, MI, 48824, USA

Abstract

We present the growth and basic magnetic and transport properties of Cr$_{1+x}$Pt$_{5-x}$P. We show that single crystals can readily be grown from a high-temperature solution created by adding dilute quantities of Cr to Pt-P based melts. Like other 1-5-1 compounds, Cr$_{1+x}$Pt$_{5-x}$P adopts a tetragonal $P4/mmm$ structure composed face-sharing CrPt$_3$ like slabs that are broken up along the $c$-axis by sheets of P atoms. EDS and X-ray diffraction measurements both suggest Cr$_{1+x}$Pt$_{5-x}$P has mixed occupancy between Cr and Pt atoms, similar to what is found in the closely related compound CrPt$_3$, giving real compositions of Cr$_{1.5}$Pt$_{4.5}$P ($x = 0.5$). We report that Cr$_{1.5}$Pt$_{4.5}$P orders ferromagnetically at $T_C = 464.5$ K with a saturated moment of $\approx 2.1 \mu_B$/Cr at 1.8 K. Likely owing to the strong spin-orbit coupling associated with the large quantity of high Z, Pt atoms, Cr$_{1.5}$Pt$_{4.5}$P has exceptionally strong planar anisotropy with estimated anisotropy fields of 345 kOe and 220 kOe at 1.8 K and 300 K respectively. The resistance of Cr$_{1.5}$Pt$_{4.5}$P has a metallic temperature dependence with relatively weak magnetoresistance. Electronic band structure calculations show that CrPt$_3$P has a large peak in the density of states near the Fermi level which is split into spin majority and minority bands in the ferromagnetic state. Furthermore, the calculations suggest substantial hybridization between Cr-3d and Pt-5d states near the Fermi level, in agreement with the experimentally measured anisotropy.

1 Introduction

From both an applied and fundamental perspective, ferromagnetism continues to provide opportunities and challenges for new research. At a practical level, the high cost and environmental concerns associated with the mining and purification of rare earth elements necessitates the search for new rare earth free permanent magnets for applications ranging from energy production, memory storage, and high performance electric engines to emerging quantum technology such as spintronics.$^{13}$ More fundamentally, it remains challenging to accurately predict the transition temperatures and even the type of magnetic order observed in many materials, especially in metallic compounds where the magnetism originates from the itinerant electrons rather than local moments.$^{14,15}$ In such itinerant ferromagnets, the physics and possible emergent phases associated with suppressing the Curie temperature towards 0 K using pressure, and/or chemical doping is less understood than for antiferromagnets and remains active frontier in condensed matter research.$^{14,15}$ These factors, amongst others, make the discovery of new, transition metal based, ferromagnetic metals highly desirable.

Recently, several new materials in the Mn(Pt,Pd)$_3$Pn (Pn = P, As) family, referred to here as 1-5-1 compounds, were discovered and found to order ferromagnetically near room temperature. Specifically, MnPt$_3$As exhibits ferromagnetic order below $T_C \approx 280$ K and MnPt$_3$P below $\approx 295$ K.$^{17,18}$ While not ferromagnetic, the isostructural materials MnPt$_5$P and FePt$_5$P have also interesting magnetic properties, as MnPt$_5$P orders antiferromagnetically at 192 K (with a small ferromagnetic, $q = 0$ component)$^{19,20}$ and FePt$_5$P is an itinerant antiferromagnet with three closely spaced transitions between 70 K and 90 K.$^{15,20}$

The magnetic 1-5-1 compounds are part of the much larger $X$(Pt,Pd)$_3$Pn family that crystallizes in the tetragonal $P4/mmm$ (#123) space group and where $X$ can be a late transition metal (Ag, Zn, Cd, Hg), a B-group element (Al–Tl), or a 3d transition metal (Mn, Fe)$^{21,22}$ The $X$(Pt,Pd)$_3$Pn materials are isostructural to the well-known family of heavy fermion superconductors CeTIn$_5$ ($T =$ Co, Rh, Ir)$^{23,24}$ and similarly to how CeTIn$_5$ can be pictured as being derived from CeIn$_3$, a useful way to describe the $X$(Pt,Pd)$_3$Pn crystal struc-
ture is as a quasi-two dimensional material formed by breaking up the parent cubic compound $X\text{Pt}_3$ into $X$-Pt layers that are separated by sheets of $P$ atoms along the $c$-axis (see Figure 1).

From the standpoint of materials discovery, the above picture is attractive given that nearly all $X$ elements that are reported to form ternary $X(\text{Pt,Pd})_3\text{Pn}$ compounds are also reported to form $X\text{Pt}_3$ binaries. With this in mind, identifying known $X\text{Pt}_3$ for which a corresponding $X\text{Pt}_3\text{Pn}$ is not yet reported may be a fruitful guide to discovering new magnetic materials. Here we focus on $X = \text{Cr}$. $\text{CrPt}_3$ is a $T_C \approx 490 \text{ K}$ ferromagnetic with among the highest magnetic anisotropy energies known for a cubic material. A high anomalous hall effect of 1750 S·cm$^{-1}$ was recently measured on $\text{CrPt}_3$ films and attributed to the Berry curvature stemming from two gaped nodal lines near the Fermi level. Based on the unique properties exhibited by $\text{CrPt}_3$, we reasoned that a hypothetical $\text{CrPt}_3\text{P}$ may also host interesting behavior.

Here, we report the discovery and basic physical properties of the compound $\text{Cr}_{1+x}\text{Pt}_{5−x}\text{P}$. We find that single crystals can readily be grown from solution by adding $\text{Cr}$ into melts based on the single phase liquid region above the $\text{Pt-P}$ eutectic composition. $\text{Cr}_{1+\frac{5}{2}}\text{Pt}_{5−\frac{5}{2}}\text{P}$ is the first ternary compound in the $\text{Cr-Pt-P}$ phase space and adopts the same tetragonal $P4/mmm$ crystal structure as the other known 1–5–1 materials. Our EDS and X-ray diffraction characterization suggests mixed occupancy between $\text{Cr}$ and $\text{Pt}$ atoms, giving true composition of $\text{Cr}_{1+x}\text{Pt}_{5−x}\text{P}$ with $x$ between 0-0.5, which is similar to what is observed in the $\text{CrPt}_3$ parent compound. The samples characterized here have $x \approx 0.5$, and we show that $\text{Cr}_{1.5}\text{Pt}_{4.5}\text{P}$ orders ferromagnetically below $T_C = 464.5 \text{ K}$ with a saturated moment of 2.1 $\mu_B$/Cr at 1.8 K. The $ab$-plane is the easy direction and the magnetic anisotropy of $\text{Cr}_{1.\frac{5}{2}}\text{Pt}_{4.\frac{5}{2}}\text{P}$ is exceptionally high, with an estimated anisotropy fields of $\approx 345$ kOe and 220 kOe at 1.8 K and 300 K respectively. Transport measurements indicate typical metallic behavior with a moderate negative magnetoresistance when the field is applied within the $ab$-plane. Density functional theory calculations show a strong peak in the density of states near the Fermi level which is split into majority and minority spin bands in the magnetic state, consistent with the picture for itinerant magnetism. Likewise, the calculations show significant hybridization between $\text{Cr}$-3d and $\text{Pt}$-5d states, which likely underpins the strong magnetic anisotropy.

2 Experimental Details

2.1 Crystal Growth

The staring materials were elemental Pt powder (Engelhard, 99.4+% purity), red $P$ (Alpha Aesar, 99.99%) and Cr pieces (Alpha Aesar, 99.999%). The elements were weighed according to a nominal molar ratio of $\text{Cr}_9\text{Pt}_{71}\text{P}_{20}$ and contained in the bottom side of a 3-piece alumina Canfield crucible set (CCS, sold by LSP Ceramics). The CCS was sealed in a fused silica ampule and was held in place with a small amount of silica wool, which serves as cushioning during the decanting step. The ampules were evacuated three times and back-filled with $\approx 1/6 \text{ atm Ar}$ gas prior to sealing.

The crystal growth took place over three steps. First, using a box furnace, the ampule was slowly warmed to $250^\circ \text{ C}$ over 6 h, then to $1180^\circ \text{ C}$ in an additional 8-12 h. After dwelling at $1180^\circ \text{ C}$ for 6 h, the furnace was cooled to $950^\circ \text{ C}$ over 40 h, after which the remaining liquid phase (a Cr-depleted, Pt-P-rich melt) was decanted by inverting the ampule into a centrifuge with specially made metal rotor and cups. After cooling to room temperature, the ampule was opened and the products found to be metallic, highly inter-grown, block-like crystals.

The remaining solidified liquid phase that was decanted and captured in the “catch” crucible of the CCS was next reused in a second step. Here, a new 3-piece CCS was assembled, using the decanted liquid in the new “growth” end. The crucible set was sealed in an ampule as described above and heated rapidly (in $\approx 2$ h) to $975^\circ \text{ C}$. After holding for 6 h, the furnace was slowly cooled to $800^\circ \text{ C}$ over 75 h and the remaining liquid again decanted. The ampule was opened to reveal a mixture of block-like crystals like those described above as well as thin, nicely formed metallic plates. In the final step, the remaining solidified liquid phase in the “catch” crucible was again reused. After evacuating and sealing into an ampule, the furnace was heated to $825^\circ \text{ C}$, held for 6 h, and then cooled to $700^\circ \text{ C}$ over 60 h where the excess liquid was decanted. The final step yielded only thin, plate-like crystals like those also found in the second step. Pictures of several plates are shown in the inset to Figure 1.

Analysis with EDS suggested that both the block-like crystals and thinner plates belonged to the same phase, with a putative chemical formula of $\text{Cr}_{1+\frac{5}{2}}\text{Pt}_{5−\frac{5}{2}}\text{P}$ (see discussion section for details). This indicates that the initial, more Cr-rich melts decanted at higher temperatures produce thicker block-like crystals, whereas using relatively Cr-depleted melts and decanting at lower temperatures results in the thinner plates. Both the three-dimensional blocks and plates were malleable, and the plates could be bent and deformed using tweezers. Furthermore, the plates could be cleaved within the basal plane. Because the block-like crystals were generally inter-grown with less clear orientation, the well formed, plate crystals were used in all following measurements.
2.2 Crystal Structure Determination

We initially attempted to use single crystal X-ray diffraction to determine the crystal structure of the plate-like crystals. Samples were analyzed with a Bruker D8 Quest Eco single-crystal X-ray diffractometer equipped with a Photon II detector and Mo radiation (λKα = 0.71073 Å). As noted above, the crystals are malleable and readily deformed, and as a result, selecting a suitable piece was challenging and the reflections were always weak and remained radiation shielding temperature homogeneity across the sample was ensured by a Cu foil. For the measurements, we used indirect geometry so that the current was applied within the ab-plane. To ensure good mechanical strength, a small portion of silver epoxy was painted over the spot-welded contacts, and typical contact resistances were ≈ 1 Ω. The transverse magnetoresistance was measured up to 90 kOe with the field applied perpendicular to the direction of current flow.

2.3 Chemical Composition

The chemical composition was 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 measurements were performed at three different positions on each crystal’s face (perpendicular to 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 crystals with unknown composition. A MnPt5P single crystal was used as a standard for Pt and P quantification, and a LaCrGe3 single crystal was used as a standard for Cr. The spectra were fitted using NIST-DTSA II Microanalysis software. The average compositions and error bars were obtained from these data, accounting for both inhomogeneity and goodness of fit of each spectra.

2.4 Physical Property Measurements

Magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System (MPMS-3) SQUID magnetometer operating in the VSM mode. For the measurements at 300–600 K, the sample was mounted on a heater stick with alumina cement, and radiation shielding temperature homogeneity across the sample was ensured by a Cu foil. For the measurements conducted at 1.8–300 K, the sample was mounted on a quartz sample holder with GE 7031 varnish. The temperature dependent measurements were carried out using a 0.5 K/min warming/cooling rate.

Resistance measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) in AC transport mode. 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 so that the current was applied within the ab-plane. To ensure good mechanical strength, a small portion of silver epoxy was painted over the spot-welded contacts, and typical contact resistances were ≈ 1 Ω. The transverse magnetoresistance was measured up to 90 kOe with the field applied perpendicular to the direction of current flow.

2.5 Electronic Band Structure Calculations

Band structure, density of states, and total energy for CrPt3P were calculated in density functional theory (DFT) using the PBEsol exchange-correlation functional with spin-orbit coupling (SOC) included. All DFT calculations were performed in VASP with a plane-wave basis set and projector augmented wave method. We used the unit cell of 7 atoms with a Γ-centered Monkhorst-Pack k-point mesh (10 × 10 × 6) k-point mesh with a Gaussian smearing of 0.05 eV. The kinetic energy cutoff was 319 eV. The ferromagnetic moment direction was changed along different axis to find the preferred direction.

3 Results and Discussion

3.1 Phase Determination and Crystal Structure of Cr1+xPt5−xP

Cr1+xPt5−xP (discussion of x in following paragraphs) is a previously unknown 1-5-1 compound that adopts a layered tetragonal crystal structure with the space group P4/mmm (123), like the previously reported XPt5P analogues. The structure is illustrated in Figure 1.

Table 1: Atomic Coordinates and Isotropic Atomic Displacement Parameters for Cr1+xPt5−xP determined by Rietveld refinement of the PXRD pattern in Figure 1b. See the text for information on refinement of the Pt site occupancy. The refinement statistics are Rwp = 11.5 and GOF = 3.2.

| Atoms | Wycoff | Occ. | x   | y   | z   | u_iso (Å²) |
|-------|--------|------|-----|-----|-----|------------|
| Pt1   | 1a     |      | 0   | 0   | 0   | 0.006(1)   |
| Pt2   | 4i     |      | 1/2 | 2   | 0   | 0.006(1)   |
| Pt3   | 1c     |      | 1/2 | 1/2 | 0   | 0.01       |
| Pt4   | 1b     |      | 0   | 0   | 1/2 | 0.01       |
and consists of slabs of face sharing CrPt$_{12}$ polyhedra that span the $ab$-plane and which are separated along the $c$ axis by sheets of P atoms. As noted in the introduction, CrPt$_5$P can also be visualized as a composite built from single layers of CrPt$_3$ (crystal structure shown in Figure 1b) in the Cu$_3$Au structure, which are separated along the $c$-axis by Pt–P–Pt slabs. This second viewpoint provides a useful lens to view the magnetic properties.

Figure 1d shows a powder X-ray diffraction pattern collected from several plate-like crystals. The Bragg peaks are somewhat broad compared to those collected on other 1-5-1 compounds, which is likely because the Cr$^{1+}_{1+x}$Pt$_{5−x}$P plates are malleable and challenging to grind into a fine powder. Nevertheless, the experimental pattern agrees well with the reflections expected from the $P4/mmm$ structure, and there are no significant peaks from secondary phases, indicating good sample purity. The lattice parameters determined from Le Bail refinements of the powder data are $a = 3.8922(2)$ Å and $c = 6.8565(1)$ Å which are very similar to those reported for MnPt$_5$P and FePt$_5$P.$^{19,20}$ The Le Bail refinement statistics are $R_{wp} = 8.66$ and GOF = 2.39, indicating a reasonable refinement.

Elemental analysis with EDS indicated that the samples are enriched with Cr and deficient in Pt compared to the expected stoichiometry of CrPt$_5$P, with true composition Cr$_{1.53(4)}$Pt$_{4.51(1)}$P$_{0.94(3)}$. The fact that the excess Cr is offset by a corresponding Pt deficiency, i.e. Cr$_{1+x}$Pt$_{5−x}$P, suggests there is mixed occupancy between Cr and Pt atoms where the Cr site is fully occupied and the extra Cr sits on the Pt sites. Considering that the parent compound CrPt$_3$ is known to form a solid solution with mixed occupancy between Cr and Pt atoms, where the Cu$_3$Au structure is maintained for compositions $\approx20–40$ % Cr, it is reasonable to believe that Cr$_{1+x}$Pt$_{5−x}$P can also accommodate excess Cr atoms on the Pt sites. Unfortunately, because the samples are malleable and easily deformed, we were unable to select a suitable, strain-free, piece for single crystal X-ray refinement (see experimental section), and the Bragg peaks were always smeared/broadened. Consequently, we were not able to satisfactorily assess the site occupancy using single crystal refinements. We next attempted Rietveld refinements of our PXRD data using the known atomic positions of the structural analogue MnPt$_5$P as starting parameters.$^{19}$ Refining the Pt occupancy $f$ gives $f_{Pt} \approx 0.9$ for both Pt sites, which is consistent with partial replacement of the Pt atoms with substantially lower Z Cr, in qualitative agreement with the Cr$_{1.5}$Pt$_{4.5}$P composition implied by the EDS analysis. We note that the thermal displacement parameters $U$ for Cr and P were fixed to 0.01 in order to ensure a stable refinement. This is likely necessary given that the large and heavy Pt atoms contribute more than 70% atomic weight in Cr$_{1+x}$Pt$_{5−x}$P and can significantly absorb X-rays. The refinements are otherwise consistent with those in other XPt$_5$P systems.$^{19,20}$ Given the limitations of our powder data, we were unable to obtain a stable refinement when explicitly attempting to model the disorder by introducing Cr onto the two Pt sites, and therefore cannot currently determine whether the excess Cr preferentially occupies one of the two Pt sites. Ultimately, our PXRD and EDS results both provide clear evidence for mixed occupancy between Cr and Pt atoms on the Pt-sublattice; however, quality single crystal diffraction data or high resolution synchrotron PXRD is needed for fully quantitative structural characterization.
3.2 Magnetic Properties of Cr$_{1+x}$Pt$_{5-x}$P

Figure 2a shows magnetization isotherms temperatures collected from 0–70 kOe and at temperatures between 1.8–300 K. Measurements were conducted on a plate-like crystal with EDS composition of Cr$_{1.5}$Pt$_{4.5}$P, and the field was applied both along the c-axis and within the ab-plane ($H \perp c$). The $M(H)$ results indicate Cr$_{1.5}$Pt$_{4.5}$P is ferromagnetic below at least 300 K with strong easy-plane anisotropy. As will be shown below, the Curie temperature is $\approx 465$ K. Full $M(H)$ loops obtained at 1.8 K and 400 K are displayed in Figure 2b and show clear hysteresis between increasing and decreasing field sweeps, confirming the ferromagnetic nature of Cr$_{1.5}$Pt$_{4.5}$P. The coercive field is $\approx 0.2$ kOe, indicating the ferromagnetism is rather soft, similar to what is observed in other 1-5-1 ferromagnets MnPd$_5$P and MnPt$_5$As, which both have small coercive fields under 50 Oe. In the H $\perp c$ orientation (i.e. with the field applied in the basal plane), the magnetization increases in a nearly step-like fashion at low fields, quickly reaching saturation by $\approx 4$ kOe, and the saturated moment falls monotonically with increasing temperature, from 2.1 $\mu_B$/Cr at 1.8 K to 1.8 $\mu_B$/Cr at 300 K. At 1.8 K, the saturated moment of $\approx 2.1$ $\mu_B$ is very close to the expected 2 $\mu_B$ for $S = 3/2$ Cr$^{3+}$.

In the magnetic hard direction ($H \parallel c$), the magnetization shows a small increase at the lowest fields and settles into a linear field dependence as $H$ approaches 70 kOe, reaching a maximum of $\approx 0.7$ $\mu_B$ at 1.8 K, which is only a third of the saturated 2.1 $\mu_B$ measured when the field is applied in the ab-plane. To determined the anisotropy fields $H_A$, we extrapolated the tangents of the $H \parallel c$ and $H \perp c$ curves to locate the field in which the respective lines meet, as shown in Figure 2a, giving an estimated $H_A$ of $\approx 345$ kOe at 1.8 K that falls monotonically with increasing temperature to $\approx 220$ kOe at 300 K. Note that all of our $M(H)$ measurements in the hard direction ($H \parallel c$) show a small low-field saturation below $\approx 2$ kOe, followed by more linear behavior at high fields. This is most likely from to a small misorientation of the sample (or part of the sample, due to malleability) such that the field is not applied exactly along the c-axis; however, at this time we cannot fully rule out the possibility of a small axial component to the ferromagnetism. Assuming the low-field saturation is from imperfect sample orientation, the anisotropy fields discussed above will slightly underestimate the true values.

Figure 3a shows the temperature dependence of the magnetization ($M/H$) measured in a $H = 1$ kOe applied field for Cr$_{1.5}$Pt$_{4.5}$P between 300–600 K. On cooling, $M/H$ increases rapidly beginning near 470 K, characteristic of the onset of ferromagnetic order. The right axis of Figure 3a shows the inverse ($M/H$)$^{-1}$ of the temperature dependent $M/H$ data above 300 K. ($M/H$)$^{-1}$ has a nearly linear, Curie-Weiss like temperature dependence above $\approx 500$ K. Curie-Weiss fits to the $H/M^{-1}$.
Figure 3: (a) Temperature dependence of $M/H$ (left axis) and $M/H^{-1}$ (right axis). The light blue line marks the Curie-Weiss fit to the high temperature data. The inset shows the temperature dependence of the spontaneous moment $M_s$ at select temperatures between 1.8-470 K, and the dashed line is an order-parameter fit (see text for more details). (b) Arrot plots between 460–470 K. The inset shows a closeup of the data between 464–466 K.

3.3 Transport properties of Cr$_{1+x}$Pt$_{5-x}$P

Figure 4a shows the temperature dependent resistance $\rho$ between 1.8–375 K. As expected, the behavior is characteristic of a metal, decreasing monotonically with cooling and approaching saturation as the lowest temperature is reached. No transitions are observed below 375 K, which is consistent with the single $T_C = 464.5$ K transition detected in the magnetic data. The residual resistance ratio $RRR = \rho(300 \text{ K})/\rho(1.8 \text{ K})$ is 16, indicating reasonably high crystal quality. Considering the mixed occupancy
between Cr and Pt atoms inferred from the EDS and X-ray diffraction analysis, 16 may appear a high RRR for a compound with such a substantial degree of crystallographic disorder (≈ 10 % of the Pt sites are occupied by excess Cr); however, the RRR of 16 is considerably lower than the RRR = 110 reported for single crystals of the structural analogue MnPt₅P₁⁸. Using a similar effective temperature below the Neel temperature still gives RRR = 70 for MnPt₅P, suggesting the atomic disorder in Cr₁₋₅Pt₄₋₅P raises the residual resistance compared to what would be expected in an ideal, disorder-free crystal.

Figure 4 shows the transverse magnetoresistance, defined as \( [R(H)−R(0)]/R(0) \), collected at 2 K with the field applied both along the c-axis and within the ab-plane. In both cases, the current flow was within the plane and the field perpendicular to the direction of the current. At 2 K and for \( H \parallel c \), CrPt₅P has a relatively small positive magnetoresistance that reaches 20 % at 9 T. When the field is applied in the ab-plane (the magnetic easy direction), the 2 K magnetoresistance first has a negative field dependence at low \( H \) that crosses over to a positive slope near ≈ 15 kOe and then increases with a similar field dependence as the \( H \parallel c \) data over the remaining range of \( H \). The negative slope at low fields is typical of ferromagnets and most likely comes from the decrease in spin disorder scattering as the field aligns the magnetic domains before crossing over to positive behavior at higher \( H \).

### 3.4 Discussion

Whereas the high Pt content and planar anisotropy likely limit the feasibility of CrPt₅P for practical applications, the 220 kOe (at 300 K) and 345 kOe (at 1.8 K) anisotropy fields are exceptionally high. For comparison, Nd₂Fe₁₄B, which is among the most widely used permanent magnets, has an anisotropy field of 82 kOe near room temperature. Other examples include MnBi \( (H_a = 50 \text{ kOe}) \), HfMnP \( (H_a = 100 \text{ kOe}) \), FePt \( (H_a = 100 \text{ kOe}) \), and CoPt \( (H_a = 140 \text{ kOe}) \). Clearly the anisotropy of CrPt₅P is substantially stronger. As magnetic anisotropy arises from spin orbit coupling, it is very likely the substantial quantity of large-Z Pt atoms in CrPt₅P underpins the high anisotropy.

The 464.5 K Curie temperature of Cr₁₋₅Pt₄₋₅P is a high ordering temperature for a compound with only 1/7 moment bearing Cr atoms per formula unit. This likely indicates that the Cr atoms do not behave as local moments and that CrPt₅P is better described as an itinerant ferromagnet in which the magnetism arises from the exchange-splitting of the conduction electrons. A simple experimental metric for evaluating the degree of itinerancy in a metallic compound is the Rhodes-Wohlfarth ratio \( q_c/q_s \), which is calculated from the high temperature effective moment and base temperature saturated moment using the following expressions:

\[
\mu_{eff}^2 = q_c(q_c + 2)^2\mu_B
\]

\[
\mu_{sat} = q_s\mu_B
\]

\[
q_c/q_s = (-1 + \sqrt{1 + (\mu_{eff}/\mu_B)^2})/(\mu_{sat}/\mu_B)
\]

For compounds with relatively low magnetic ordering temperatures, high ratios suggest itinerant behavior, and \( q_c/q_s \) should be close to unity when the magnetism is local moment like (i.e. in rare-earth containing materials). The Rhodes-Wohlfarth ratio also converges towards 1 in itinerant magnets when the ordering temperatures is high (> 300 K)¹⁰. For Cr₁₋₅Pt₄₋₅P, we find \( q_c/q_s = 1.3 \), which is consistent with the expectation for an itinerant magnetic with a relatively high, 465 K, Curie temperature. Because \( q_c/q_s \) of 1 are also expected for local moment systems, which may be consistent with the trivalent oxidation state of Cr implied by the magnetic measurements, this result is ultimately somewhat ambiguous; however, the band structure calculations discussed below also support itinerant, Stoner-like magnetism.

To provide greater insight into the magnetism and strong anisotropy measured in CrPt₅P, we used density functional theory (DFT) to calculate the electronic band structure, which is displayed in Figure 5. Our calculations considered the ideal 1-5-1 composition, i.e. without excess Cr and mixed occupancy between Cr and Pt atoms. Consistent with the experimental results, the calculations show CrPt₅P to be a metal with many well dispersed bands crossing the Fermi level \( (E_F) \). The orbital projected density of states (PDOS) for nonmagnetic and ferromagnetic (with the moment along the a-axis) phases of CrPt₅P are respectively given in Figures 5a and 5b. In both cases, the majority of the states near \( E_F \) are derived from Cr-3d and Pt-5d orbitals. The main contributions from P orbitals are significantly deeper in energy, with a band of P-3p based states from -10 to -5 eV and the P-3s states spanning -14 to -13 eV.

Comparing the density of states calculations for nonmagnetic and ferromagnetic CrPt₅P, we observe a narrow peak in the DOS around the Fermi level in the paramagnetic phase. The spike in DOS is composed primarily of Cr-3d orbital states with a smaller but still substantial contribution from Pt-5d orbitals, suggesting the hybridization between Cr-3d and Pt-5d orbitals in CrPt₅P is strong. As magnetic anisotropy arises from spin orbit coupling, the substantial hybridization between Cr-3d and the high Z Pt-5d states at \( E_F \) is consistent with the strong magnetic anisotropy observed experimentally. Once in the ferromagnetic state, the peak at \( E_F \) is split, where the lower spin majority band is approximately centered at \( E_F \) and the higher spin minority band at 2 eV. Both upper and lower peaks retain significant contributions from both Cr-3d and Pt-5d orbital states. The calculations shown in Figures 5a and 5b match what is anticipated for an itinerant ferromagnet, where a locally high density of states near \( E_F \) is split into upper and lower, majority and minority, spin bands by the on-site Coulomb repulsion, giving rise to a net magnetization.
Figure 5: (a) Electronic band structure for CrPt$_5$P in the ferromagnetic phase (with moments along the a-axis). (b) Density of states in the non-magnetic phase. (c) Density of states in the ferromagnetic phase. The calculations assume the ideal 1-5-1 composition (no Cr-Pt site disorder)

Our calculations therefore support CrPt$_5$P as an itinerant ferromagnet, which is consistent with its Rhodes-Wohlfarth ratio and high Curie temperature.

Integrating the contributions of the spin up and down electrons, we calculated a magnetic moment of 3.2 $\mu_B$/Cr, which is in good agreement with the experimental $\mu_{eff} \approx 3.5$ $\mu_B$/Cr inferred from the Curie-Weiss fits. Moreover, the calculations indicate the most favorable ferromagnetic configuration is with the ordered moment within the ab-plane, consistent with the experimental observations, and we calculate a magnetic anisotropy energy -1.261 meV/f.u. Although this suggests weaker anisotropy than the experimental results, the DFT calculations overall satisfactorily capture the magnetism experimentally observed in CrPt$_5$P.

Because the Cr$_{1+x}$Pt$_{5-x}$P studied here deviate from the ideal stoichiometry, with $x \approx 0.5$, we also constructed a (2x2x1) supercell with two Pt sites, one at 4i and the other at 1a, substituted by Cr, in order to preliminarily study the effect of excess Cr on the electronic structure. The calculations indicate that excess Cr placed on either Pt sites prefers to couple antiferromagnetically with the host Cr; however, the additional Cr changes the DOS away from $E_F$ at +2.0 eV and -1.0 eV, and we find that the DOS near $E_F$ is not strongly altered by the presence of excess Cr. Consequently, it is unclear from these calculations how strongly the excess Cr will alter the magnetism. In our experimental $M(H)$ data, we observe no evidence for a ferrimagnetic state associated with AFM coupling between Cr moments associated with the different crystallographic positions, and the saturated moments are in reasonable agreement with the expectations for trivalent Cr, both suggesting Cr$_{1.5}$Pt$_{4.5}$P shows simple ferromagnetic order. A more detailed study on the effect of mixed occupancy requires configurational thermodynamics using cluster expansion method or coherent potential approximation, ideally in tandem with measurements on crystals with different compositions ($x$).

As described in the discussion of the crystal structure, Cr$_{1+x}$Cr$_{5-x}$P can be envisioned as single layers of CrPt$_3$ that span the ab-plane and which are divided along the c-axis by planes of P atoms. From this perspective, it is interesting to compare the magnetic properties of Cr$_{1.5}$Cr$_{5-x}$P with those of the parent compound CrPt$_3$. In CrPt$_3$, the Cr atoms also order ferromagnetically with a Curie temperature of $\approx 490$ K [27,30]. In Cr$_{1+x}$Cr$_{5-x}$P, the insertion of the layer of P atoms nearly doubles the Cr-Cr distance along the c-axis from 3.874 Å in CrPt$_3$ to 6.857 Å in CrPt$_5$P, whereas the in-plane Cr-Cr distances (the a-lattice parameters) are approximately the same in each compound. Considering that the salient structural feature of face sharing Cr-Pt polyhedra is conserved in both compounds, and that the electronic states near the Fermi level in CrPt$_5$P are essentially derived only from Cr and Pt based orbital states, the similar magnetic properties suggests that the underlying physics governing the magnetism in each compound may be sim-
ilar and that the addition of the P-layer in Cr$_{1+x}$Cr$_{5-x}$P serves to weaken the exchange interaction between magnetic moments and slightly lower the ordering temperature. As Cr$_{1+x}$Cr$_{5-x}$P and CrPt$_3$ share similar crystallographic and magnetic properties, investigation of topological transport properties, like the high anomalous hall effect found in CrPt$_3$, may be an attractive future direction for work on Cr$_{1+x}$Cr$_{5-x}$P.

4 Summary and Conclusions

We grew single crystals of Cr$_{1+x}$Pt$_{5-x}$P ($x = 0.5$) and found that it is a remarkably anisotropic ferromagnet with a $T_C = 464.5$ K and a 1.8 K anisotropic field of 345 kOe. We show that single crystals can readily be grown out ternary Cr-Pt-P solutions. Like all other members of the $X$($Pt,Pd$)$_5$P family, Cr$_{1+x}$Pt$_{5-x}$P crystallizes in the $P4/mmm$ space group and is comprised of CrPt$_3$-like layers spaced out by sheets of P atoms along the $c$-axis. Our EDS and XRD analysis indicate Cr-enrichment, likely pointing toward site occupancy disorder and true compositions of Cr$_{1.5}$Pt$_{4.5}$P, which is similar to the disorder found in the parent compound CrPt$_3$. Likely owing to the high Pt content, CrPt$_5$P has very strong magnetic anisotropy in which the $ab$-plane is the easy direction. The estimated anisotropy fields are $\approx 345$ kOe and 220 kOe respectively at 1.8 K and 300 K. Cr$_{1.5}$Pt$_{4.5}$P exhibits metallic transport behavior and has relatively weak transverse magnetoresistance. Electron band structure calculations are consistent with itinerant magnetism, showing the CrPt$_5$P has a local peak in the density of states near the Fermi level that is split into upper and lower bands in the ferromagnetic state. Likewise, our calculations suggest strong hybridization between Cr-3d and Pt-5d states, in agreement with the experimentally observed strong magnetic anisotropy.

Acknowledgements

Work at Ames National Laboratory was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Ames National Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. TJS, PCC, and LLW were supported by the Center for Advancement of Topological Semimetals (CATS), an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences, through Ames National Laboratory under its Contract No. DE-AC02-07CH11358 with Iowa State University. W.X. is supported by NSF-DMR-2053287.

Conflicts of Interest

The authors have no conflicts of interest to declare.

*corresponding authors’ email: slade@ameslab.gov, canfield@ameslab.gov

References

(1) Herbst, J. F. R$_2$Fe$_{14}$B materials: Intrinsic properties and technological aspects. Rev. Mod. Phys. 1991, 63, 819–898.

(2) Coey, J. M. D. Hard Magnetic Materials: A Perspective. IEEE Transactions on Magnetics 2011, 47, 4671–4681.

(3) Weller, D.; Moser, A.; Folks, L.; Best, M. E.; Lee, W.; Toney, M. F.; Schwierct, M.; Thiele, J.-U.; Doerner, M. F. High $K_r$ Materials Approach to 100 Gbits/in$^2$. IEEE Transactions on Magnetics 2000, 36, 10–15.

(4) Victora, R.; Shen, X. Exchange coupled composite media for perpendicular magnetic recording. IEEE Transactions on Magnetics 2005, 41, 2828–2833.

(5) Shiroishi, Y.; Fukuda, K.; Tagawa, I.; Iwasaki, H.; Takenori, S.; Tanaka, H.; Mutoh, H.; Yoshikawa, N. Future options for HDD storage. IEEE Transactions on Magnetics 2009, 45, 3816–3822.

(6) Felser, C.; Fecher, G. H.; Balke, B. Spintronics: a challenge for materials science and solid-state chemistry. Angewandte Chemie International Edition 2007, 46, 668–699.

(7) Stoner, E. C. Collective electron ferromagnetism. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences 1938, 165, 372–414.

(8) Wohlfarth, E. XLI. Collective electron ferromagnetism: Rectangular energy bands. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 1951, 42, 374–390.

(9) Landrum, G. A.; Dronskowski, R. The orbital origins of magnetism: from atoms to molecules to ferromagnetic alloys. Angewandte Chemie International Edition 2000, 39, 1560–1585.

(10) Takahashi, Y., Spin Fluctuation Theory of Itinerant Electron Magnetism; Springer: Berlin, Germany, 2013; Vol. 9.

(11) Brando, M.; Belitz, D.; Grosche, F. M.; Kirkpatrick, T. R. Metallic quantum ferromagnets. Rev. Mod. Phys. 2016, 88, 025006.

(12) Kaluarachchi, U. S.; Bud’ko, S. L.; Canfield, P. C.; Taufour, V. Tricritical Wings and Modulated Magnetic Phases in LaCrGe$_3$ Under Pressure. Nature Communications 2017, 8, 1–6.

(13) Gati, E.; Wilde, J. M.; Khasanov, R.; Xiang, L.; Dissanayake, S.; Gupta, R.; Matsuda, M.; Ye, F.; Haberl, B.; Kaluarachchi, U.; McQueney, R. J.; Kreysig, A.; Bud’ko, S. L.; Canfield, P. C. Formation of short-range magnetic order and avoided ferromagnetic quantum criticality in pressurized LaCrGe$_3$. Phys. Rev. B 2021, 103, 075111.
(14) Kirkpatrick, T. R.; Belitz, D. Ferromagnetic Quantum Critical Point in Noncentrosymmetric Systems. Phys. Rev. Lett. 2020, 124, 147201.

(15) Xiang, L.; Gati, E.; Bud’ko, S. L.; Saunders, S. M.; Canfield, P. C. Avoided ferromagnetic quantum critical point in pressurized La5Co2Ge3. Phys. Rev. B 2021, 103, 054419.

(16) Shen, B.; Zhang, Y.; Komijani, Y.; Nicklas, M.; Borth, R.; Wang, A.; Chen, Y.; Nie, Z.; Li, R.; Lu, X., et al. Strange-metal behaviour in a pure ferromagnetic Kondo lattice. Nature 2020, 579, 51–55.

(17) Gui, X.; Xie, W. Crystal structure, magnetism, and electronic properties of a rare-earth-free ferromagnet: MnPt5As. Chemistry of Materials 2020, 32, 3922–3929.

(18) 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, e202000145.

(19) Gui, X.; Klein, R. A.; Brown, C. M.; Xie, W. Chemical Bonding Governs Complex Magnetism in MnPt5P. Inorganic Chemistry 2020, 60, 87–96.

(20) Gui, X.; Marshall, M.; Dissanayaka Mudiyanselage, 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 FePt5P. ACS Applied Electronic Materials, 3.

(21) El-Boragy, M.; Schubert, K. Über eine verzerzte dichteste Kugelpackung mit Leerstellen/On a Deformed Close-Packed Structure Containing Constitutional Vacancies. International Journal of Materials Research 1970, 61, 579–584.

(22) Zakharova, E. Y.; Kazakov, S. M.; Götze, A.; Kohlmann, H.; Kuznetsov, A. N. Ternary palladium-indium-phosphorus and platinum-indium-phosphorus compounds based on the Cu3Au-type: Structure, bonding, and properties. Journal of Solid State Chemistry 2018, 265, 266–273.

(23) Hegger, H.; Petrovic, C.; Moshopoulou, E. G.; Hundley, M. F.; Sarrao, J. L.; Fisk, Z.; Thompson, J. D. Pressure-Induced Superconductivity in Quasi-2D CeRhIn5. Phys. Rev. Lett. 2000, 84, 4986–4989.

(24) Petrovic, C.; Pagliuso, P.; Hundley, M.; Movshovich, R.; Sarrao, J.; Thompson, J.; Fisk, Z.; Monthoux, P. Heavy-fermion superconductivity in CeCoIn5 at 2.3 K. Journal of Physics: Condensed Matter 2001, 13, L337.

(25) Petrovic, C.; Movshovich, R.; Jaime, M.; Pagliuso, P.; Hundley, M.; Sarrao, J.; Fisk, Z.; Thompson, J. A new heavy-fermion superconductor CeIrIn5: A relative of the cuprates? EPL (Europhysics Letters) 2001, 53, 354.

(26) Movshovich, R.; Jaime, M.; Thompson, J.; Petrovic, C.; Fisk, Z.; Pagliuso, P.; Sarrao, J. Unconventional Superconductivity in CeIrIn5 and CeCoIn5: Specific Heat and Thermal Conductivity Studies. Physical Review Letters 2001, 86, 5152.

(27) Pickart, S.; Nathans, R. Neutron Diffraction Investigation of Pt-Based Alloys of the First Transition Series. Journal of Applied Physics 1963, 34, 1203–1204.

(28) Besnus, M.; Meyer, A. Magnetic properties of the ordered and disordered CrPt3 and CrPt phases. physica status solidi (b) 1973, 58, 533–542.

(29) Maruyama, H.; Matsuoka, F.; Kobayashi, K.; Yamazaki, H. A separation of the Pt 5d orbital and spin moments in a ferrimagnetic CrPt3 compound. Physica B: Condensed Matter 1995, 208, 787–788.

(30) Leonhardt, T.; Chen, Y.; Rao, M.; Laughlin, D.; Lambeth, D.; Kryder, M. CrPt3 thin film media for perpendicular or magneto-optical recording. Journal of Applied Physics 1999, 85, 4307–4309.

(31) Goto, T. Effects of the Atomic Environment on the Magnetic Properties of Cr-Pt Alloys. Journal of the Physical Society of Japan 1977, 43, 1848–1853.

(32) Markou, A.; Gayles, J.; Derunova, E.; Svecik, P.; Noky, J.; Zhang, L.; Ali, M. N.; Sun, Y.; Felser, C. Hard magnet topological semimetals in XPt3 compounds with the harmony of Berry curvature. Communications Physics 2021, 4, 1–7.

(33) 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.

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

(35) Canfield, P. C. New materials physics. Reports on Progress in Physics 2019, 83, 016501.

(36) Canfield, P. C.; Fisk, Z. Growth of single crystals from metallic fluxes. Philosophical Magazine B 1992, 65, 1117–1123.

(37) 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.

(38) Newbury, D. E.; Ritchie, N. W. In Scanning Microscopies 2014, 2014; Vol. 9236, pp 90–106.
(39) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Physical Review* 1964, 136, B864.

(40) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140, A1133–A1138.

(41) 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.

(42) 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.

(43) 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.

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

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

(46) Arrott, A. Criterion for Ferromagnetism from Observations of Magnetic Isotherms. *Phys. Rev.* 1957, 108, 1394–1396.

(47) Bolzoni, F.; Moze, O.; Pareti, L. First-order field-induced magnetization transitions in single-crystal Nd$_2$Fe$_{14}$B. *Journal of Applied Physics* 1987, 62, 615–620.

(48) McGuire, M. A.; Cao, H.; Chakoumakos, B. C.; Sales, B. C. Symmetry-lowering lattice distortion at the spin reorientation in MnBi single crystals. *Phys. Rev. B* 2014, 90, 174425.

(49) Lamichhane, T. N.; Taufour, V.; Masters, M. W.; Parker, D. S.; Kalharachchi, U. S.; Thimmaiah, S.; Bud’ko, S. L.; Canfield, P. C. Discovery of ferromagnetism with large magnetic anisotropy in ZrMnP and HfMnP. *Applied Physics Letters* 2016, 109, 092402.

(50) Inoue, K.; Shima, H.; Fujita, A.; Ishida, K.; Oikawa, K.; Fukamichi, K. Temperature dependence of magnetocrystalline anisotropy constants in the single variant state of L$_{10}$-type FePt bulk single crystal. *Applied Physics Letters* 2006, 88, 102503.

(51) Shima, H.; Oikawa, K.; Fujita, A.; Fukamichi, K.; Ishida, K.; Nakamura, S.; Nojima, T. Magnetocrystalline anisotropy energy in L1$_0$-type CoPt single crystals. *Journal of Magnetism and Magnetic Materials* 2005, 290, 566–569.

(52) Rhodes, P.; Wohlfarth, E. P. The effective Curie-Weiss constant of ferromagnetic metals and alloys. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 1963, 273, 247–258.