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Magnetic order in the $S_{\text{eff}} = 1/2$ triangular-lattice compound NdCd_3P_3

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We present and characterize a new member of the RCd_3P_3 (R = rare earth) family of materials, NdCd_3P_3 , which possesses Nd^{3+} cations arranged on well-separated triangular lattice layers. Magnetic susceptibility and heat capacity measurements demonstrate a likely $S_{\text{eff}} = 1/2$ ground state, and also reveal the formation of long-range antiferromagnetic order at $T_N = 0.34$ K. Via measurements of magnetization, heat capacity, and electrical resistivity, we characterize the electronic properties of NdCd_3P_3 and compare results to density functional theory calculations.

INTRODUCTION

Crystalline compounds possessing geometric magnetic frustration remain at the forefront of research in condensed matter physics, owing to the plethora of interesting ground states they may harbor. Confinement in low-dimensional cases, such as quasi-one-dimensional systems and two-dimensional structures, can often result in enhanced quantum fluctuations capable of rendering unique quantum ground states, such as the quantum spin liquid state [1–3]. Materials systems possessing two-dimensional triangular lattices have, in particular, attracted much attention owing to the large degree of geometric frustration ensured by a two-dimensional array of edge-sharing triangles of magnetic moments, which further enhances quantum fluctuations and increases the likelihood of unconventional quantum ground states. Indeed, several triangular lattice quantum spin liquid candidates have been identified, such as those with transition metal cations such as NaRuO_2 [4], and rare-earth cations such as NaYbSe_2 [5–7], YbMgGaO_4 [8–10], and NaYbO_2 [11–13].

The layered RM_3Pn_3 (R = rare earth; M = Zn, Cd; Pn = P, As) family of pnictide compounds is one that hosts R^{3+} cations on well-separated triangular lattice layers [14, 15]. These compounds have interlayer distances on the order of 10 Å, and magnetic interactions are thus expected to be highly-two-dimensional, thus theoretically enhancing quantum fluctuations. However, the rare-earth cations are octahedrally coordinated by pnictide anions, which act as strong crystal field ligands and can have a substantial impact on the crystal field interactions of the $4f$ electrons and result in strong anisotropies that can modify frustration. The impact of crystal field anisotropies on the magnetic properties of CeCd_3P_3 and CeCd_3As_3 have recently been explored, and these anisotropies have been suggested as a primary mechanism for the emergence of magnetic order in these

systems below $T_N = 0.42$ K [16], despite the aforementioned two-dimensionality.

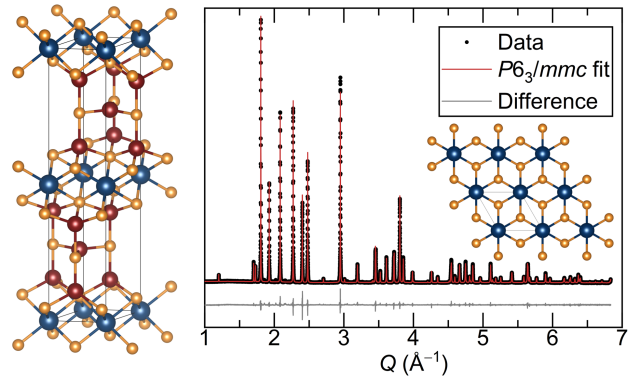


FIG. 1. Crystal structure and synchrotron X-ray diffraction pattern of NdCd_3P_3 , collected at $T = 300$ K at 11-BM. Maroon atoms are Nd, blue atoms are Cd and orange atoms are P.

The RM_3Pn_3 family of materials is quite extensive, and many rare-earth variants (from $R = \text{La}$ to Er) have been found for the RZn_3P_3 subclass [14]. For the RCd_3P_3 subclass, only $R = \text{La}$, Ce , and Pr have been reported [14, 17]. Previous measurements on LaCd_3P_3 and CeCd_3P_3 demonstrated metallic states in single-crystalline samples with an unknown, possibly structural, transition at $T = 170$ K and 126 K, respectively [17]. In contrast, polycrystalline samples displayed insulating behavior [18]. In addition, for the RZn_3P_3 compounds, an increasing tendency toward metallicity appears with increasing R radius, which points toward a likely balance between unit cell volume and band dispersion near the Fermi level [19]. Thus, exploring the RCd_3P_3 materials class as well as the overall RM_3Pn_3 phase space may provide an avenue toward the systematic control of metallicity in these two-dimensional, naively frustrated, magnetic materials.

In this article, we report the structural and electronic properties of NdCd_3P_3 , a new member of the RCd_3P_3 family of materials. We find that it is isostructural to previously-reported LaCd_3P_3 and CeCd_3P_3 variants. We further report that NdCd_3P_3 is an electrical insulator with a charge transport gap of $E_G = 0.60$ eV, in agree-

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ment with density functional theory calculations predicting an insulating state. Despite the aforementioned large atomic distances between Nd^{3+} triangular layers, our measurements of heat capacity and magnetic susceptibility reveal a magnetic ordering transition at $T_C = 0.34$ K, which is nearly equivalent to the mean-field magnetic interaction strength derived from fits to the susceptibility data to Curie-Weiss law, $\Theta_W = -0.39$ K.

METHODS

Polycrystalline samples of RCd_3P_3 were prepared using conventional solid state synthetic techniques. First, lanthanide monophosphide RP precursors were prepared by direct reaction of elemental rare earth powders (Fisher Scientific, 99.9% REO) with red phosphorus (BeanTown Chemical, 99.9999%). Stoichiometric amounts of the elements were weighed and ground together in an argon-filled glovebox, followed by heating in alumina crucibles at 850 °C for 48 hours in sealed, evacuated silica ampoules. These precursors were then combined with a stoichiometric amount of Cd_3P_2 (Alfa Aesar, 99.5% metals basis), and ball milled in a Spex 8000D Mixer/Mill for one hour using a tungsten carbide vial and tungsten carbide balls. The milled mixture was then sealed in evacuated silica tubes and heated to 800 °C for 24 hours before being quenched in water.

High resolution synchrotron powder X-ray diffraction (XRD) data were collected at the 11-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory, using an incident wavelength of 0.475799 Å. Data were collected at $T = 300$ K. Powder XRD data were also collected using a laboratory x-ray source, a Panalytical Empyrean diffractometer employing $\text{Cu K}\alpha$ X-rays in a Bragg-Brentano geometry. Rietveld refinements of the data were performed using the TOPAS Academic software package.

Magnetic susceptibility measurements were carried out in a Quantum Design Magnetic Property Measurement System (MPMS3), as well as using a vibrating sample mode (VSM) option on a Quantum Design 14 T Dynacool Physical Property Measurement System (PPMS). Resistivity and heat capacity measurements were performed using the PPMS using heat capacity and electrical transport options. Heat capacity measurements between $T = 0.1$ and 2 K were performed using a Quantum Design dilution refrigerator.

First-principles electronic structure calculations based on density functional theory (DFT) were performed using the Elk code. This code is an all-electron, full-potential linearized augmented plane wave (LAPW) code with local orbitals (LO). Calculations were performed using the PBEsol exchange functional [20], and included spin-orbit coupling. Calculations for NdCd_3P_3 included a Hubbard U term ranging from 4.5 - 6.5 eV, applied to the $\text{Nd}^{3+} 4f$ states. Calculations were also performed using the Vienna ab Initio Simulation Package (VASP) ver-

sion 5.4.4. All calculations employed the Perdew-Burke-Ernzerhof (PBE) functional and projector-augmented wave potentials.

RESULTS AND DISCUSSION

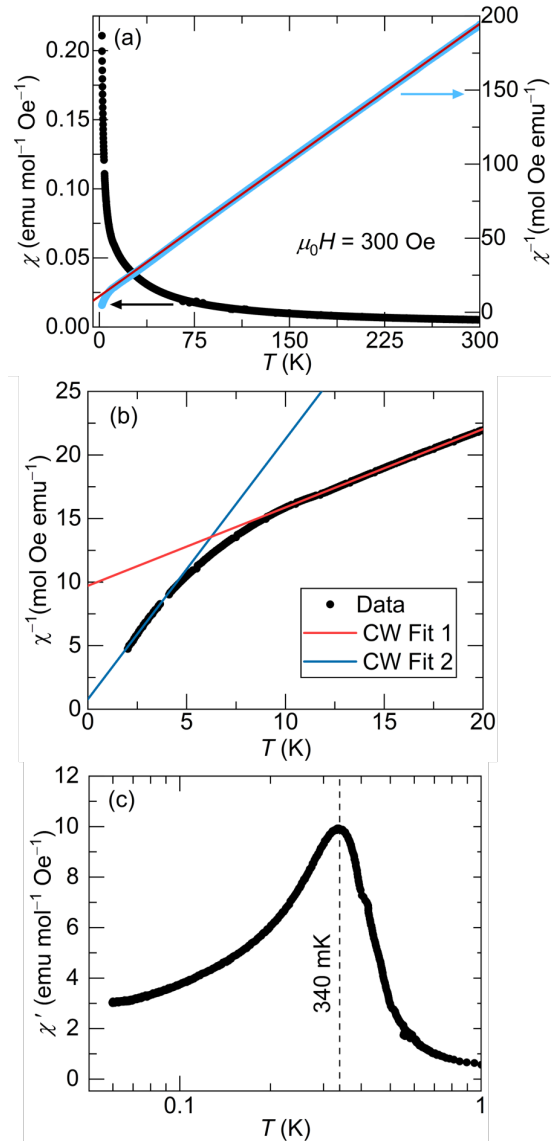


FIG. 2. **A.** DC magnetic susceptibility of NdCd_3P_3 , demonstrating full Curie-Weiss behavior between $T = 50 - 300$ K. Inset shows no bifurcation of zero-field cooled vs. field cooled data sets. **B.** Low temperature Curie-Weiss fits, demonstrating two regions, likely due to crystal field depopulation. **C.** AC susceptibility data collected between $T = 0.06$ and 2 K, demonstrating an ordering transition centered around $T = 340$ mK.

Synchrotron powder XRD data are shown in Figure 1, and structural parameters can be found in the supplementary information[21]. NdCd_3P_3 is isostructural to LaCd_3P_3 and CeCd_3P_3 , which have been previously re-

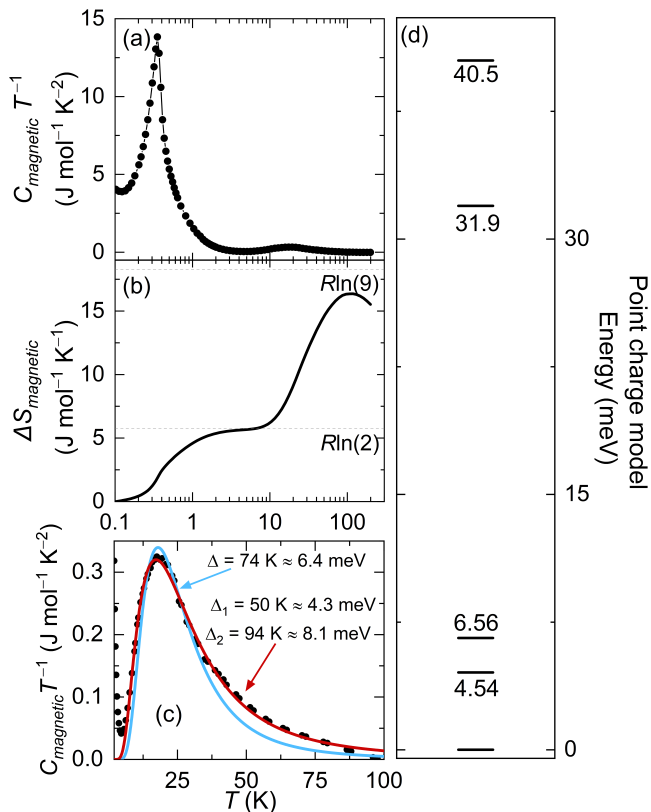


FIG. 3. A. Magnetic heat capacity for NdCd_3P_3 , extracted by subtracting a scaled LaCd_3P_3 diamagnetic analogue data set. B. Change in magnetic entropy of NdCd_3P_3 , which plateaus near $\text{Rln}(2)$ at low temperature before reducing toward zero at the ordering transition. C. Predicted crystal field levels as extracted using a point charge model.

ported to crystallize in the hexagonal, $P6_3/mmc$ ScAl_3C_3 structure type [22]. NdCd_3P_3 is layered, and layers of edge-sharing NdP_6 octahedra are separated 10.46 Å away from each other by Cd_3P_3 layers. These cadmium phosphide layers are built up of tetrahedral, corner-sharing CdP_4 units, and trigonal planar CdP_3 units. The large separation between magnetic Nd^{3+} layers by many nonmagnetic atoms should naively promote a dominant two-dimensional exchange coupling within the triangular lattice planes.

The DC magnetic susceptibility of NdCd_3P_3 is shown in Figure 2. It follows Curie-Weiss behavior between $T = 50 - 300$ K, and fits yield an effective, local Nd^{3+} moment of $p_{\text{eff}} = 3.62$. The high temperature local moment is consistent with the expected $p_{\text{eff}} = 3.62$ for a free Nd^{3+} $j = 9/2$ ion with a Landé $g = 8/11$. No irreversibility is observed between zero-field cooled (ZFC) and field-cooled (FC) data down to 2 K, implying an absence of any spin freezing in this temperature range.

At low temperatures, the magnetic susceptibility deviates from the high-temperature, fixed moment Curie-Weiss behavior, likely due to the depopulation of low-lying Nd^{3+} crystal field states, as shown in Figure 2 (b).

The deviation starts below $T = 50$ K, in agreement with heat capacity data discussed later in this paper. Once the low-lying excited states are depopulated upon cooling, the lowest temperature region can then be refit to a new Curie-Weiss model with an effective Nd^{3+} moment of $1.98 \mu_B$. In this low temperature regime, the mean field is antiferromagnetic and $\Theta_W = -0.38$ K, consistent with the ordering temperature observed in both AC susceptibility and heat capacity measurements as discussed below.

Figure 2 (c) displays the ac susceptibility data collected down to 60 mK. Upon cooling below 2 K, the susceptibility continues to diverge in the condensed $S_{\text{eff}} = 1/2$ ground state and peaks at $T_N = 340$ mK before rapidly decreasing. This is consistent with an antiferromagnetic ordering transition arising at the same mean-field Θ_W value determined from the temperature Curie-Weiss fit in the crystal field ground state. No systematic frequency dependence can be observed in the ac susceptibility data, as demonstrated in the supplementary information [21].

Heat capacity data were also collected on NdCd_3P_3 from $T = 80$ mK to 300 K, and identical measurements were performed on LaCd_3P_3 , which was then used to subtract off the lattice contribution. Figure 3 (a) shows the remaining magnetic contribution to the heat capacity where two main features are observed: a peak with a maximum at $T = 340$ mK, and a second, broader feature centered around $T = 18$ K. The sharp peak represents a transition into a magnetically ordered state, as also suggested by the AC susceptibility data (see Figure 2 (c)). This ordering temperature is consistent with the extracted Weiss temperature of $\Theta_W = -0.38$ K. Based on the negative Weiss temperature, it suggests that this peak is a sign of an antiferromagnetic ordering transition.

Turning to the second, higher temperature peak in the magnetic heat capacity, the feature is highlighted in Figure 3 (c). This asymmetric peak can be fit with both a two-level and a three-level Schottky anomaly model, yielding gaps of $\Delta_{\text{Schottky}} = 6.4$ meV for the two-level and $\Delta_{\text{Schottky}}^1 = 4.3$ meV and $\Delta_{\text{Schottky}}^2 = 8.1$ meV for the three-level model. While both models have comparable statistics, a three-level Schottky anomaly both qualitatively fits the data better, and is in agreement with Nd^{3+} point charge calculations shown in Figure 3 (c). These calculations were performed using the PyCrystal-Field package [23], and assumed +3 charges for Nd cations and -3 for P anions, and employed the Rietveld-derived crystal structure of NdCd_3P_3 with experimental Nd-P bond distances. The integrated magnetic entropy is plotted in Figure 3 (b) and shows a gradual reduction of entropy on cooling across the Schottky anomaly and a plateau around $T = 10$ K at $\text{Rln}2$, both consistent with an $S_{\text{eff}} = 1/2$ magnetic ground state.

Figure 4 shows the electrical resistivity of a sintered pellet of NdCd_3P_3 in the range $T = 250 - 400$ K. The resistivity increases with decreasing temperature, implying a bulk insulating state. The data was fit to a number of exponentially activated functions with varying b ex-

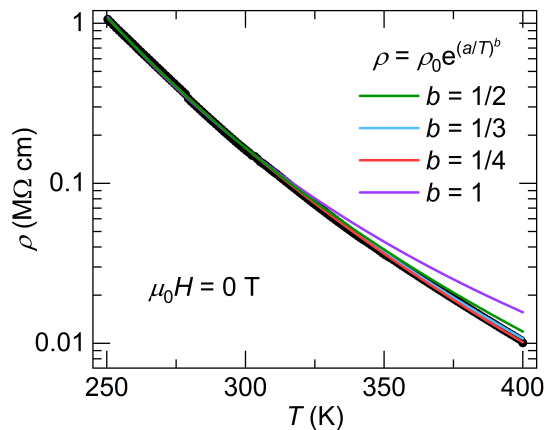


FIG. 4. The measured electrical resistivity of NdCd_3P_3 . The data was fit to various models of variable-range hopping transport, and found to be best fit using either $b = 1/3$ or $b = 1/4$ exponents, indicating either two- or three-dimensional hopping. The extracted band gap from the exponentially activated fit at lower temperatures ($b = 1$) is $E_{gap} = 0.66(2)$ eV.

ponents, which indicate either purely exponentially activated behavior ($b = 1$) or variable range hopping behavior ($b > 1$). In the case of NdCd_3P_3 , the data is best fit to a variable range hopping model where the exponent can be fit to either $b = 1/3$ or $b = 1/4$, which represent two-dimensional and three-dimensional hopping, respectively [24, 25]. The distinction between the two is made difficult due to the fact that the sample is polycrystalline. The NdCd_3P_3 transport gap E_{gap} was extracted from a fit to the low temperature data using the exponentially activated Arrhenius form $\rho = \rho_0 e^{a/2k_B T}$, where a is the band gap and is on the order of $0.66(2)$ eV. This is consistent with trends from earlier work, which demonstrated polycrystalline samples of other RCd_3P_3 compounds to be insulators [18]. In addition, E_{gap} for NdCd_3P_3 is smaller than E_{gap} for LaCd_3P_3 (0.73 eV) and CeCd_3P_3 (0.75 eV) [18]. This follows the same trend as the RZn_3P_3 series of compounds, where the charge transport behavior goes from insulating to metallic across the lanthanides [19], and therefore the band gaps are expected to become smaller when employing higher atomic mass lanthanides. In contrast, however, single crystals of LaCd_3P_3 and CeCd_3P_3 show metallic behavior with a carrier density on the order of 10^{20} carriers/cm³, as well as anomalies in the electrical transport behavior that are mirrored in the heat capacity [17]. Neither the weakly metallic behavior nor the thermodynamic/transport anomalies reported in $(\text{La,Ce})\text{Cd}_3\text{P}_3$ are observed in polycrystalline samples of NdCd_3P_3 .

In order to understand the discrepancy in physical properties observed in NdCd_3P_3 compared to LaCd_3P_3 and CeCd_3P_3 , we performed electronic band structure calculations using density function theory (DFT). The electronic band structures of LaCd_3P_3 and NdCd_3P_3 are shown in Figure 5. Spin-orbit coupling was included in these calculations, as well as a Hubbard U term for the

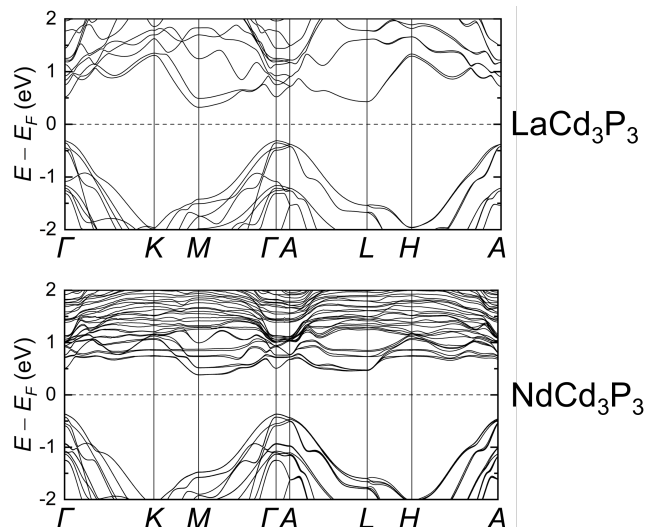


FIG. 5. The electronic band structures of LaCd_3P_3 and NdCd_3P_3 . Calculations include spin-orbit coupling. In both cases, the valence band maximum is made up nearly entirely of P-p states, whereas the conduction band minima are La or Nd d -bands. The Nd f -states can be found in the conduction band.

Nd- f states, $U_{\text{eff}} = 5$ eV. This is the lowest U_{eff} value required to fully gap out the Nd-4 f states that would otherwise be present at the Fermi level, as shown in the supplementary information for this manuscript [21].

Our calculations demonstrated that both LaCd_3P_3 and NdCd_3P_3 are gapped, with calculated indirect band gaps of 0.75 eV and 0.63 eV, respectively. These values are in rough agreement with the transport gaps derived from resistivity measurements [18], and suggest that the metallicity observed in studies of single crystals [17] results from light doping. Given that the valence band maximum is primarily composed of disperse P p -bands and the conduction band minimum is composed of rather localized R d -bands, the doped carriers in metallic samples are more likely to be holes. This is confirmed by a positive field-dependence of the Hall coefficient as previously reported in LaCd_3P_3 and CeCd_3P_3 [17].

CONCLUSION

In this report, we synthesized polycrystalline samples of a new member of the RCd_3P_3 family of compounds, NdCd_3P_3 . We find NdCd_3P_3 crystallizes in the ScAl_3C_3 structure and susceptibility data show that the compound realizes a $S_{\text{eff}} = 1/2$ magnetic ground state. Heat capacity and AC susceptibility measurements reveal the onset of magnetic order below $T = 340$ mK at a temperature consistent with the antiferromagnetic Weiss field in this system. Charge transport data reveals that NdCd_3P_3 is insulating with an E_{gap} of 0.66 eV, in good agreement with DFT calculations.

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