Magnetic transitions in the 1D chain compounds NdPd₅Ge₃ and NdPt₅Ge₃

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Abstract
We present the structural and initial magnetic characterization of the previously unreported materials NdPd₅Ge₃ and NdPt₅Ge₃. These materials, with one-dimensional Nd chains, crystallize in the orthorhombic YNi₅Si₃-type structure in space group Pnma. Magnetic ordering is observed for both compounds at ∼2.2 K for NdPd₅Ge₃ and ∼3.0 K for NdPt₅Ge₃.

A magnetic-field-induced transition is clearly observed for NdPd₅Ge₃ below 2 K, at an applied magnetic field of around 1.6 T. The heat capacity data reveals that essentially all the available magnetic entropy is released at the magnetic ordering transition for NdPd₅Ge₃ but that only 29% is seen for NdPt₅Ge₃ at temperatures down to 1.5 K, the data implying that a second magnetic transition can be expected at lower temperatures.

Keywords: rare earth magnetic ordering, one-Dimensional Nd chain, field-induced magnetic transition

(Some figures may appear in colour only in the online journal)

1. Introduction

Rare-earth-based intermetallics have attracted interest due in large part to their magnetic properties, which often reflect different degrees of hybridization between the rare earth f electrons and the other atomic orbitals present. Intriguing electronic and magnetic properties, such as heavy-fermion superconductivity, long-range magnetic ordering, and Kondo insulator behavior have been observed in such systems [1–9]. In addition, materials containing heavy elements with strong spin–orbit coupling, like Pd and Pt, are of interest due to such atom’s ability to polarize, split or invert energy bands, such as has been observed in topological materials [10–12].

Motivated by these considerations, we here report the synthesis, structure, and magnetic characterization of NdPd₅Ge₃ and NdPt₅Ge₃. The cerium analogs, CePd₅Ge₃ and CePt₅Ge₃, which are isostructural, antiferromagnetically order (1.9 K for CePd₅Ge₃ and 1.1 K for CePt₅Ge₃) with possible low-dimensional magnetism observed for the latter [13–16]. For CePt₅Ge₃, a tail in the specific heat was observed, indicating antiferromagnetic short-range correlations of a low-dimensional character above the 3D long-range order [16]. Moreover, magnetic-field-induced magnetic transitions were observed in CePd₅Ge₃—two successive transitions, a spin–flop transition and an AFM to paramagnetic state transition can be seen when magnetic field is applied along a direction close to b axis [15]. We find that the Nd-based materials show slightly higher magnetic ordering temperatures than do their less strongly magnetic Ce analogs and other differences in the magnetism. Of interest from the structural viewpoint in these materials are the well separated one-dimensional (1D) chains made from the rare-earth atoms. Our magnetic characterization shows that the two new materials studied have similar magnetic properties, and suggest that those properties may be very sensitive to the spin–orbit coupling differences between Pd and Pt.

2. Experiment

The arc melting method, under a high purity Zr-gettered, argon atmosphere, was employed to synthesize polycrystalline samples of both materials. Elemental palladium (99.95%, APS 0.5–1.7 micron, Alfa Aesar) and platinum (>99.98%, ~60 mesh, Alfa Aesar) were first pressed into pellets and arc melted. PdGe and PtGe precursors were then made by
arc melting the pre-melted Pd/Pt chunks with germanium (≥99.9999%, pieces, Alfa Aesar) in a molar ratio of 1:1.02 to compensate for the mass loss of Ge. Finally, the ternary NdM5Ge3 materials were synthesized by mixing elemental Nd (≥99%, ingot, Beantown Chemical), the PdGe/PtGe precursors and pre-melted Pd or Pt in the molar ratio of 1:3:2.1. The mixture was arc melted three times with the melted buttons turned over between melts. The final products are air-stable. A Bruker D8 advance eco diffractometer with Cu Kα radiation and a LynxEye-XE detector was employed to obtain the powder x-ray diffraction (PXRD) patterns for both materials at ambient temperature. The patterns were fitted by the Rietveld method in Fullprof using as an initial guess the crystal structure obtained from the inorganic crystal structure database for CePd5Ge3 [13].

The DC magnetic susceptibility data were obtained by utilizing a dynacool physical property measurement system (PPMS, Quantum design Inc.) in the temperature range of 1.8 K–300 K, and, when necessary, under different applied magnetic fields. The magnetic susceptibility was defined as $\frac{M}{H}$ where $H$ is the applied magnetic field in Oe and $M$ is the measured magnetization in emu. Heat capacity was measured using a standard relaxation method in the PPMS between 1.5 K to 10 K with the $^3$He function.

### Table 1. Rietveld fitting parameters from the ambient temperature PXRD patterns of NdPd5Ge3 and NdPt5Ge3 space group Pnma (No. 62).

| Material   | Rp (%) | Rwp (%) | Rexp (%) | χ² |
|------------|--------|---------|----------|----|
| NdPd_{5}Ge_{3} | 6.67   | 9.05    | 7.13     | 1.61 |
| NdPt_{5}Ge_{3} | 6.63   | 8.80    | 6.40     | 1.89 |

### 3. Results

#### 3.1. Crystal structure

The PXRD patterns of NdPd$_5$Ge$_3$ and NdPt$_5$Ge$_3$ fit well to the model CePd$_5$Ge$_3$ structure, as shown in figures 1(a) and (b). The materials obtained have high purity. The Rietveld fitting parameters and refined atomic positions are listed in tables 1(a) and 2. The materials are isostructural with CePd$_5$Ge$_3$ [13], which crystallizes in the orthorhombic YNi$_5$Si$_3$-type structure with space group Pnma (No. 62). In our materials, replacing the Pd with Pt increases $a$, $b$ and $c$ by 0.3%, 0.5% and 0.2%, respectively.

As is shown in figure 2(a), the structure consists of rare-earth-based Nd@Ge$_6$ prisms imbedded in a framework of Pd or Pt-based M@Ge$_4$ tetrahedra and M@Ge$_5$ pyramids. The
Table 2. Structural parameters determined at ambient temperature for NdPd$_5$Ge$_3$ and NdPt$_5$Ge$_3$. In space group Pnma (No. 62) with cell parameters $a = 20.1788$ (4) Å, $b = 4.1066$ (1) Å, $c = 7.2555$ (1) Å for NdPd$_5$Ge$_3$ and $a = 20.2457$ (3) Å, $b = 4.1289$ (1) Å, $c = 7.2686$ (1) Å for NdPt$_5$Ge$_3$.

|        | $x_{\text{Nd}}$ | $y_{\text{Nd}}$ | $z_{\text{Nd}}$ |
|--------|-----------------|-----------------|-----------------|
| NdPd$_5$Ge$_3$ |                 |                 |                 |
| Nd1    | 0.1431 (2)      |                 | 0.876 (1)       |
| Pd1    | 0.2798 (3)      | 0.868 (1)       |                 |
| Pd2    | 0.4961 (2)      | 0.374 (1)       |                 |
| Pd3    | 0.0152 (3)      | 0.622 (1)       |                 |
| Pd4    | 0.1147 (2)      | 0.364 (1)       |                 |
| Pd5    | 0.2949 (4)      | 0.069 (1)       |                 |
| Ge1    | 0.4174 (4)      | 0.109 (2)       |                 |
| Ge2    | 0.2386 (4)      | 0.385 (2)       |                 |
| Ge3    | 0.4176 (3)      | 0.662 (1)       |                 |
| NdPt$_5$Ge$_3$ |                 |                 |                 |
| Nd1    | 0.1446 (4)      |                 | 0.881 (1)       |
| Pt1    | 0.2986 (3)      | 0.681 (1)       |                 |
| Pt2    | 0.4911 (2)      | 0.365 (1)       |                 |
| Pt3    | 0.0211 (3)      | 0.622 (1)       |                 |
| Pt4    | 0.1180 (3)      | 0.354 (1)       |                 |
| Pt5    | 0.2954 (3)      | 0.090 (1)       |                 |
| Ge1    | 0.415 (1)       | 0.104 (2)       |                 |
| Ge2    | 0.2508 (6)      | 0.363 (2)       |                 |
| Ge3    | 0.418 (1)       | 0.590 (1)       |                 |

Table 3. Nd–Nd distances for NdPd$_5$Ge$_3$ and NdPt$_5$Ge$_3$ at ambient temperature.

|        | $d_1$ (Å) | $d_2$ (Å) | $d_3$ (Å) |
|--------|-----------|-----------|-----------|
| NdPd$_5$Ge$_3$ | 6.0003 (4) | 6.3856 (4) | 4.107 (1) |
| NdPt$_5$Ge$_3$ | 5.9730 (4) | 6.4469 (4) | 4.129 (1) |

Figure 2. (a) The crystal structure of NdPd$_5$Ge$_3$ and NdPt$_5$Ge$_3$. Red, blue and gray balls represent Nd, Pd or Pt (M) and Ge atoms. (b) The M@Ge$_6$ ($n = 4$ or 5) polyhedra and Nd@Ge$_8$ prisms in the structure. (c) The Nd chains looking down the $b$ axis (from a slightly skewed angle to facilitate visualization of the chains). The symbols $d_1$, $d_2$ and $d_3$ are the shortest distances between the Nd chains within the $ac$-plane.

Nd atoms form one-dimensional (1D) chains along the crystallographic $b$ axis. The coordination polyhedra are shown in figure 2(b). The symmetry equivalent chains in the structure are arranged along the $a$ axis in a staggered fashion. In figure 2(c), which shows the Nd atoms only, the Nd–Nd distances are marked as $d_1$, $d_2$ and $d_3$, which are the shortest Nd–Nd bond lengths within and between the different Nd chains. For both compounds, $d_1$ is the same as $d_2$ while $d_3$ is larger. As shown in table 3, the Nd–Nd distance within the chains is 0.5% longer in NdPd$_5$Ge$_3$ than in NdPt$_5$Ge$_3$.

3.2. Magnetic properties

3.2.1. NdPd$_5$Ge$_3$. As illustrated in figure 3(a), under an applied external field of 0.3 T, Curie–Weiss (CW) behavior is found for NdPd$_5$Ge$_3$ in the temperature range of 25 K–300 K. The data can be fit with the CW law: $\chi = C/(T - \theta_{\text{CW}})$ where $\chi$ is the measured magnetic susceptibility of the material, $C$ is independent of temperature, related to the effective moment, and $\theta_{\text{CW}}$ is the CW theta (temperature independent contributions to the magnetic susceptibility are not significant in magnitude in these materials). In NdPd$_5$Ge$_3$, $\theta_{\text{CW}}$ is $-6.41$ (1) K and the effective moment $\mu_{\text{eff}} = \sqrt{3C} = 3.71 \mu_B$/f.u., which is close to the expected effective moment of the free Nd$^{3+}$ ion (3.62 $\mu_B$). To better visualize the low-temperature magnetic behavior of this material, $\chi$ vs $T$ curves under an applied field of 50 Oe, measured in both the zero-field cooling (ZFC) and field cooling (FC) modes, are presented in figure 3(b). The shape of the FC curve at low temperature suggests ferromagnetic (FM) ordering. A drop of susceptibility was found at $\sim 2.2$ K for the ZFC curve which we attribute to the movement of magnetic domain walls. The inset of figure 3(b) presents the first derivative of the $\chi$ vs $T$ curve (d$\chi$/dT for the ZFC mode), which reveals that non-CW behavior starts from $\sim 3.5$ K, as indicated by the divergence of the d$\chi$/dT curve from d$\chi$/dT = 0.

Figures 3(c) and (d) show the hysteresis loops for NdPd$_5$Ge$_3$ in various field ranges at various temperatures. In the low-field region ($\sim 0.05$ T–$0.05$ T), the magnetization for this material reflects the presence of a small FM component ($\sim 0.39 \mu_B$/Nd$^{3+}$) at 1.8 K at temperatures below 3 K. A coercive field around of 20 Oe can be seen at 1.8 K, indicating FM ordering. Above 3 K, the FM contribution vanishes, which reveals that the moments in NdPd$_5$Ge$_3$ are not aligned ferromagnetically above 3 K. Thus, the observed low field FM component is a consequence of the ordered state in NdPd$_5$Ge$_3$ instead of the presence of trace elemental FM impurities. Below $T_M$, a magnetic-field-induced transition is observed at $\sim 1.6$ T. In the inset of Figure 3(c), we enlarge the magnetization curve from 1 T to 3 T at 1.8 K and 2 K to illustrate this. After the spontaneous magnetization at low field ($\ll 1$ T), the magnetization curves at both 1.8 K and 2 K continue to increase in a nearly linear way until the magnetic field of $\sim 1.6$ T, where both curves undergo a transition to different slopes, i.e., a different magnetic state. As can be seen in inset of figure 3(d), broad peaks indicating the likely presence
3.2.2. \( \text{NdPt}_5\text{Ge}_3 \). The temperature-dependent magnetic susceptibility for \( \text{NdPt}_5\text{Ge}_3 \) can be seen in figure 4(a). CW behavior is also observed in this case. The CW temperature from the CW fit, \( \theta_{\text{CW}} \), is \(-5.69 \) (4) K, while the effective moment is \( \sim 3.76 \mu_B \) per Nd atom, similar to what is observed for the Pd variant. When the external magnetic field is smaller, i.e., 50 Oe, \( \text{NdPt}_5\text{Ge}_3 \) exhibits a broader magnetic ordering transition than is seen for \( \text{NdPd}_5\text{Ge}_3 \), at \( \sim 3.0 \) K. The inset of figure 4(b) shows the first derivative of \( \chi \) vs \( T \) measured in the ZFC mode of a field-induced transition to a different magnetic state are observed in the first derivative curves between 1 and 3.5 T at 1.8 K and 2 K, while at 2.5 K, no such transition is observed up to fields of 7 T. At higher applied fields, the magnetization of \( \text{NdPd}_5\text{Ge}_3 \) saturates at 1.8 K with moment at 9 T \( M \sim 1.93 \mu_B/\text{Nd}^{3+} \), which is smaller than the saturated moment for \( \text{Nd}^{3+} \). Thus, by 9 T, three f electrons on Nd are not totally aligned by the field.

3.3. Heat capacity

Figure 5 describes the heat capacity behavior of both compounds from 1.5 K to 10 K. The total heat capacity of a magnetic material can be interpreted as the sum of electronic plus phonon plus magnetic contributions, as for \( C_{\text{total}} = C_{\text{elect}} + C_{\text{phonon}} + C_{\text{mag}} \). Due to the lack of non-magnetic model of such system, the electronic contribution could be described

![Figure 3](image-url)
Figure 4. (a) Temperature-dependence of the magnetic susceptibility ($\chi$), and $1/\chi$ of NdPt$_5$Ge$_3$ between 1.8 K and 300 K under applied magnetic field of 0.3 T measured in the ZFC mode. The cyan line represents the CW fitting. (b) (Main panel) Temperature-dependence of magnetic susceptibility ($\chi$) of NdPt$_5$Ge$_3$ between 1.8 K and 10 K under an applied magnetic field of 50 Oe (0.005 T). (Inset) First derivative of $\chi$ vs $T$ obtained in the ZFC mode from 2 K to 6 K. (c) (Main panel) Hysteresis loops of NdPt$_5$Ge$_3$ from $-9$ T to 9 T at multiple temperatures. (Inset) Zoom-in of the hysteresis loop at 1.8 K between $-0.1$ T and $0.1$ T. (d) (Main panel) Hysteresis loops of NdPt$_5$Ge$_3$ from $-0.2$ T to 0.2 T at low temperatures. (Inset) Zoom-ins of hysteresis loops at 4 K, 5 K, 6 K and 8 K from $-0.01$ T to 0.01 T.

Figure 5. (Main panel) Heat capacity of (a) NdPd$_5$Ge$_3$; (b) NdPt$_5$Ge$_3$ from 1.5 K to 10 K. Solid blue circle with line represents $C_{\text{total}}/T$ while empty blue circle with line stands for $C_{\text{magnon}}/T$. Red and orange solid lines indicate $(C_{\text{phonon}} + C_{\text{electron}})/T$ and entropy change from magnetic ordering ($\Delta S_{\text{magnon}}$). Dashed magenta line is the value of $R \ln 2$. The entropy change from magnetic ordering of NdPd$_5$Ge$_3$ was plotted natural logarithmically to make the figure clear. (Inset) Temperature-dependence of total heat capacity of (a) NdPd$_5$Ge$_3$; (b) NdPt$_5$Ge$_3$ from 1.5 K to 10 K.
as \( C_{\text{elect}} = \gamma T \) where \( \gamma \) is the Sommerfeld coefficient while the phonon contribution could be estimated by using \( C_{\text{phonon}} = \beta T^3 \) according to Debye formula where \( \beta \) is the electronic contribution coefficient [17]. However, the \( T^3 \) relation cannot lead to a good fitting, thus a \( T^2 \) term was added. Therefore, the non-magnetic contributions can be estimated by using a polynomial fit to the temperatures above the magnetic transition: 
\[
C_{\text{electron+phonon}} = \gamma T + \beta_1 T^2 + \beta_2 T^4
\]
where \( a, b_1 \) and \( b_2 \) are constants and were fitted to 1.18 (2), −0.015 (1), 0.000 10 (1) for NdPt\(_5\)Ge\(_3\) and 0.036 (6), 0.0085 (2), −0.000 021 (2) for NdPt\(_5\)Ge\(_3\). After extraction of the approximate electronic and phononic contributions, the residual heat capacity can be attributed to the magnetic system only. As shown in figure 5(a), a sharp peak can be found for NdPt\(_5\)Ge\(_3\) at around 2.5 K and that the entropy does not saturate until 3.5 K. Meanwhile, the entropy change, \( \Delta S_{\text{magnon}} \), exceeds the value of \( R \ln 2 \) at 2.6 K while reveals that most entropy change from magnetic ordering can be found below 2.6 K, i.e., the system is fully magnetic ordered by that temperature. However, in figure 5(b), even though a low broad peak is observed at around 3 K, the total entropy change is only \( \sim 29\% \) of \( R \ln 2 \), which indicates that most of the entropy from magnetic ordering in NdPt\(_5\)Ge\(_3\) cannot be seen above 1.5 K, i.e., the magnetic system is not fully ordered down to that temperature. Considering the fact that the total heat capacity of NdPt\(_5\)Ge\(_3\) increases dramatically by 1.5 K, a large magnetic entropy change may be observed below 1.5 K.

4. Conclusion

We have synthesized two previously unreported magnetic Nd-based materials, NdPd\(_5\)Ge\(_3\) and NdPt\(_5\)Ge\(_3\). The phases are pure and their crystal structures, determined by PXRD, are very similar to that of CePd\(_5\)Ge\(_3\) [13], suggesting that this structure is stable for germanides for at least the larger rare earths. Initial magnetic characterization of both materials shows magnetic ordering at 3 K or below, with field-induced magnetic state transitions for NdPd\(_5\)Ge\(_3\) at field of \( \sim 1.6 \) T. Heat capacity data shows sharp magnetic ordering with most entropy change appearing above 1.5 K for NdPd\(_5\)Ge\(_3\). However, even though a broad peak is found in the heat capacity at \( \sim 3 \) K for NdPt\(_5\)Ge\(_3\), the entropy sum is only \( \sim 23\% \) of \( R \ln 2 \), indicating that by 1.5 K, NdPt\(_5\)Ge\(_3\) does not show complete magnetic ordering. Our data reveal that the magnetic structures of these phases are rather complex, and thus neutron diffraction study would be needed for full characterization.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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