A comparison of the structure and localized magnetism in Ce₂PdGa₁₂ with the heavy fermion CePdGa₆

Robin T. Macaluso, Jasmine N. Millican, Satoru Nakatsuji, Han-Oh Lee, B. Carter, Nelson O. Moreno, Zachary Fisk, Julia Y. Chan

Abstract

Single crystals of Ce₂PdGa₁₂ have been synthesized in Ga flux and characterized by X-ray diffraction. This compound crystallizes in the tetragonal P4/nbm space group, Z = 2 with lattice parameters of a = 6.1040(2) Å and c = 15.5490(6) Å. It shows strongly anisotropic magnetism and orders antiferromagnetically at T_N ~ 11 K. A field-induced metamagnetic transition to the ferromagnetic state is observed below T_C. Structure–property relationships with the related heavy-fermion antiferromagnet CePdGa₆ are discussed.

Keywords: Heavy fermion; Metamagnet; CePdGa₆; Ce₂PdGa₁₂; Single crystal; Intermetallics

1. Introduction

Ce-based intermetallic compounds have attracted interest because of their variety of electronic properties. Extensive studies have been performed to understand so-called “heavy fermion” states at low temperatures where large values of magnetic susceptibility and electronic specific heat are observed as a result of f-electrons coupling with conduction electrons [1]. The search for new layered materials is important in exploring new heavy fermion superconductors and in deepening our understanding of the role of structural dimensionality. This is indeed the case for the highest T_c to date, of a Ce-based heavy fermion superconductor, which is found in the layered CeCoIn₅ (T_c = 2.3 K) [2].

We have previously reported the synthesis and structure of a new Ce-based layered intermetallic compound, CePdGa₆, and its La-analog [3]. CePdGa₆ exhibits heavy fermion behavior with a specific heat coefficient γ ~ 230–400 mJ/mol-Ce K². It shows highly anisotropic magnetism and orders antiferromagnetically at T_N ~ 5.5 K. The layered nature of the crystal structure, consisting of face-sharing CeGa₈/₄ and edge-sharing PdGa₈/₂ rectangular prisms alternating in a 1:1 ratio along the c-axis, is consistent with anisotropy observed in the magnetism. In the CeGa₈/₄ layers, Ce is coordinated to 8 Ga atoms at the corners of rectangular prisms, forming face-sharing rectangular prisms. Meanwhile, the PdGa₈/₂ layers consist of edge-sharing rectangular prisms with Pd at the center and Ga atoms at the corners.

In our search for new layered materials in ternary Ce–Pd–Ga system, we have discovered a new phase, Ce₂PdGa₁₂. The tetragonal structure is composed of Ce–Ga and PdGa₈/₂ layers, similar to CePdGa₆. Magnetic and specific heat measurements suggest an antiferromagnetic (AF) ground state of Ce₂PdGa₁₂, whose spin configuration transforms from a collinear AF to a canted one on lowering temperature. Moreover, we have found a field-induced metamagnetic transition in the AF state. We will discuss the structure–property relationships with the related heavy-fermion antiferromagnet CePdGa₆.
2. Experimental

2.1. Synthesis

Single-phase crystals of La$_2$PdGa$_{12}$ and Ce$_2$PdGa$_{12}$ were obtained by using flux growth methods. La or Ce ingot (3N, Ames Laboratory), Pd (5N, Alfa Aesar), and Ga (5N, Alfa Aesar) were placed into an alumina crucible in a 1:1:20 ratio. The contents were sealed into an evacuated fused silica tube, and the ampoule was heated to 1423 K for 2 h and allowed to cool to 723 K at a rate of 8 K/h, at which point the ampoules were immediately inverted and spun with a centrifuge. Plate-like single crystals were mechanically extracted. Typical crystal size ranged between 0.125 and 1 cm$^3$. No noticeable degradation of the crystals in air was observed.

Single-phase crystals of LaPdGa$_6$ and CePdGa$_6$ were obtained by similar methods. La or Ce ingot (3N, Ames Laboratory), Pd (5N, Alfa Aesar), and Ga (5N, Alfa Aesar) were placed into an alumina crucible in a 1:1:20 ratio. After sealing the contents into a fused silica tube, the ampoule was heated to 1423 K for 2 h and allowed to cool quickly to 773 K at a rate of 150 K/h. The samples were then slow cooled at a rate of 8 K/h to 673 K, at which point the ampoules were immediately inverted and spun with a centrifuge. Single crystals were mechanically extracted. Flux growth methods using a 1:1:20 ratio of Ce:Pd:Ga and a heat treatment up to 1423 K followed by cooling at a rate of 8 K/h and centrifugation at 623 K yielded a mixture of CePdGa$_6$ and Ce$_2$PdGa$_{12}$.

2.2. X-ray diffraction

A suitable 0.03 $\times$ 0.03 $\times$ 0.08 mm$^3$ silver-colored fragment of Ce$_2$PdGa$_{12}$ was mounted onto the goniometer of a Nonius KappaCCD diffractometer equipped with MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data were collected up to $\theta = 30.00^\circ$ at 293 K. A similar treatment was applied to a 0.05 $\times$ 0.08 $\times$ 0.08 mm$^3$ silver-colored fragment of La$_2$PdGa$_{12}$. Further crystallographic parameters for Ce$_2$PdGa$_{12}$ and its La analog are provided in Table 1. The space group and atomic positions from Sm$_2$NiGa$_{12}$ were used as an initial structural model for the structure determination of both La$_2$PdGa$_{12}$ and Ce$_2$PdGa$_{12}$ compounds. The structural model was refined using SHELXL97 [4]. Data were corrected for extinction and refined with anisotropic displacement parameters. Data were also corrected for absorption by a multi-scan method using HKL Scalepack. Atomic positions and displacement parameters for both compounds are provided in Table 2, and selected interatomic distances are provided in Table 3. To ensure homogeneity and sample quality, single-crystal X-ray diffraction was performed on several single crystals from multiple batches of samples. Single-crystal X-ray diffraction experimental results are consistent with the temperature schemes to obtain single-phase CePdGa$_6$ and Ce$_2$PdGa$_{12}$.

2.3. Physical property measurements

Magnetization data were obtained using a Quantum Design Magnetic Property Measurement System SQUID magnetometer. The temperature-dependent magnetization data were obtained first under zero-field cooled (ZFC)
conditions from 2 to 330 K under a field of 0.1 T. Magnetization was then measured upon heating to obtain field-cooled (FC) data after cooling to 2 K under field. Field (H)-dependent measurements were collected at 2 K with H swept between 0 and 5.5 T. These procedures were followed for crystallographic ab-plane of the crystal aligned parallel and perpendicular to the magnetic field. The specific heat was measured by a thermal relaxation method from 20 to 0.35 K at zero magnetic field and ambient pressure using a Quantum Design Physical Property Measurement system. The entropy was obtained by integrating the specific heat divided by the temperature with respect to the temperature.

3. Results and discussion

3.1. Structure

The structure of Ce₂PdGa₁₂ is shown in Fig. 1 and is isostructural to Sm₂NiGa₁₂ [5]. Single crystals of Ce₂PdGa₁₂ crystallize in the tetragonal space group, P4/nbm (No. 125 with origin choice 2), Z = 2. The Ce, Pd, Ga1, Ga2, Ga3, and Ga4 atoms occupy the 4h, 2c, 4g, 4g, 8m, and 8m sites, respectively.

The structure can be viewed as Ce atoms residing in Ga cavities of a three-dimensional network of [PdGa]. The [PdGa] subunit can then be further divided into PdGa₆ segments and Ga-only segments. Within the PdGa₆ segment, there are slightly distorted PdGa₆(1/2) rectangular prisms, where the Pd atom is coordinated to eight Ga atoms: four Ga₃ atoms with interatomic distances of 2.5512(10) Å and four other Ga₃ atoms by 2.5558(10) Å. These distances are typical of Pd–Ga bonds in Pd₅Ga₃ [6], PdGa₅, Pd₂Ga [7], and in CePdGa₆ [3] where the bonding distances range between 2.388 and 2.701 Å. In addition, the sum of the two covalent radii of Ga (1.25 Å) and Pd (1.28 Å) is 2.53 Å [8], which is close to our experimental

| Table 3
Selected interatomic distances (Å) of La₃PdGa₁₂ and Ce₂PdGa₁₂ |
|------------------------|------------------------|
|                         | La₃PdGa₁₂              | Ce₂PdGa₁₂             |
|                         | La layer               | Ce layer              |
|                         |                         |                       |
|                         | La–Ga1 (× 4)           | Ce–Ga1 (× 4)          |
|                         | 3.2047(6)              | 3.2033(5)             |
|                         | La–Ga4 (× 2)           | Ce–Ga4 (× 2)          |
|                         | 3.2331(15)             | 3.2286(13)            |
|                         | La–Ga3 (× 2)           | Ce–Ga3 (× 2)          |
|                         | 3.2784(13)             | 3.2772(11)            |
|                         | La–Ga3 (× 2)           | Ce–Ga3 (× 2)          |
|                         | 3.2824(13)             | 3.2808(11)            |
|                         | PdGa₆ segment          | PdGa₆ segment         |
|                         | Ga1–Ga3 (× 4)          | Ga1–Ga3 (× 4)         |
|                         | 2.6283(10)             | 2.6257(10)            |
|                         | Pd–Ga3 (× 4)           | Pd–Ga3 (× 4)          |
|                         | 2.5570(13)             | 2.5512(10)            |
|                         | (× 4)                  | (× 4)                 |
|                         | 2.5519(12)             | 2.5558(10)            |
|                         | Ga-only segment        | Ga-only segment       |
|                         | Ga2–Ga4 (× 4)          | Ga2–Ga4 (× 4)         |
|                         | 2.6204(11)             | 2.6173(10)            |
|                         | Ga4–Ga4 (× 1)          | Ga4–Ga4 (× 1)         |
|                         | 2.5260(3)              | 2.5290(2)             |

Fig. 1. The crystal structure of Ce₂PdGa₁₂ along the c-axis is shown with Ce as black-filled circles, Pd as gray-filled circles, and Ga as white circles. The structure can be viewed as Ce contained in Ga cavities alternating with Ga-only segments and PdGa₆ segments. Dashed lines represent the unit cell.
radius of Ga [8]. These distances in the PdGa\(_{8/2}\) rectangular prisms are similar to the PdGa\(_{8/2}\) prisms in CePdGa\(_6\) where the Ga–Ga interatomic distance is shorter along the c-axis (2.7299(19) Å) and longer across the ab-plane (3.076(1) Å).

To illustrate the striking resemblance between the two structures, the structure of CePdGa\(_6\) and the structure of Ce\(_2\)PdGa\(_{12}\), are presented in Fig. 2. The unit cell of CePdGa\(_6\), which is shown as solid lines in Fig. 2a, can be viewed as a primitive unit cell with Ce at the origin. Pd atoms bisect each of the edges along the c-axis, and two Ga layers—each consisting of either Ga1 or Ga3—separate the Ce and Pd atoms. Fig. 2b shows that there is a similar packing arrangement found in Ce\(_2\)PdGa\(_{12}\). In fact, Ce\(_2\)PdGa\(_{12}\) can be viewed as CePdGa\(_6\) units (shown as solid lines) alternating with Ga-only segments along the c-axis.

The Ga-only segment consists of two Ga layers; one layer is composed of Ga2 and the other of Ga4. The Ga2 sheet includes Ga2–Ga2 contact distances ranging between 4.3176(3) and 6.1060(4) Å, indicating that the Ga2 atoms are isolated from each other. The Ga4–Ga4 atoms, however, are separated by 2.5290(2) Å, similar to 2.50 Å, the bonding distance by summing two Ga covalent radii (1.25 Å) [8]. Ga4 atoms also form interatomic distances of 2.6173(10) Å with Ga2 atoms, falling within the range of 2.297–2.930 Å found in CeGa\(_6\) [9], CeGa\(_2\) [9], and PdGa\(_5\) [7].

Fig. 3 shows the local Ce coordination of Ce\(_2\)PdGa\(_{12}\). Using a Ce–Ga bonding cutoff of \(~\)3.3 Å, which is larger than the projected sum of 2.9 Å of the Ce (1.65 Å) and Ga (1.25 Å) covalent radii [8], the Ce atom is coordinated to 10 Ga atoms: 4 Ga1, 4 Ga3, and 2 Ga4 whereas Ce is coordinated to 8 Ga atoms in CePdGa\(_6\). All of these Ce–Ga distances are similar to Ce–Ga bond distances found in the binary compounds, CeGa\(_2\) [9] and CeGa\(_6\) [9], which range between 3.252 and 3.299 Å. As shown in Fig. 3, the Ce atom caps a rectangular antiprism composed of Ga1 and Ga3 atoms. The Ce–Ga1 and Ce–Ga3 distances are 3.2034(5) Å and 3.2772(11) Å, respectively. In addition, Ce is also bonded to two Ga4 atoms with an interatomic distance of 3.2286(13) Å. Rare-earth atoms can be found as the cap of main group layers, such as in CeNiSb\(_3\) [3,10], (RE)In\(_{1–x}\)Sb\(_2\) (RE = La–Nd) [11], (RE)MSb\(_3\) (M = V, Cr) [12], and RESb\(_2\) [13,14]. The Ga1 and Ga3 atoms surrounding Ce can be viewed as two different layers, where the Ga4 layer also serves as the face of the PdGa\(_{8/2}\) rectangular prisms. Although the Ga1–Ga1 interatomic distance is greater than 4 Å and indicates that intralayer Ga1 interactions are unlikely, the distance between Ga1 and Ga3 layers of 2.6257(10) Å implies that there may be some weak interlayer interactions.

### 3.2. Magnetism

In order to compare the magnetic data of CePdGa\(_6\) and Ce\(_2\)PdGa\(_{12}\), we have re-measured the magnetization on single crystals of single-phase CePdGa\(_6\) and Ce\(_2\)PdGa\(_{12}\). Previous magnetic data of CePdGa\(_6\) [3] apparently has a
Ce₂PdGa₁₂ inclusion. The temperature dependence of the susceptibility \( \chi \) is given for Ce₂PdGa₁₂ and CePdGa₆ in Figs. 4a and b, respectively. The field of 0.1 T was applied along \( ab \)-plane and \( c \)-axis. In Ce₂PdGa₁₂, data for both orientations follow Curie–Weiss behavior above 100 K. The effective moments, \( \mu_{\text{eff}} \), are estimated to be 2.54 \( \mu_B \) (\( ab \)-plane) and 2.59 \( \mu_B \) (\( c \)-axis), very similar to the expected Ce \( J = \frac{5}{2} \) local moment, \( \mu_{\text{eff}} = 2.54 \mu_B \) (\( ab \)-plane) and 2.45 \( \mu_B \) (\( c \)-axis), with \( \theta = -12.9 \) K (\( ab \)-plane) and -1.17 K (\( c \)-axis), suggesting antiferromagnetic interactions. Single-crystal neutron diffraction experiments are in progress to determine the magnetic structures for CePdGa₆ and Ce₂PdGa₁₂.

The field dependence of the magnetization \( M \) for Ce₂PdGa₁₂, as shown in Fig. 5, was measured under fields along the \( c \)-axis and \( ab \)-plane. Interestingly, the \( c \)-axis magnetization shows a jump at 2.5 T, after showing a linear increase with the field. This indicates a metamagnetic transition, most likely due to a spin-flip transition from an antiferromagnetic to a ferromagnetic state. Along the crystallographic \( ab \)-plane, on the other hand, \( M \) increases rapidly up to \( B = 1 \) T and reaches the value \( \sim 0.2 \mu_B \) at 5 T. A small hysteresis is observed below 0.1 T at 2 K, indicating the system has a ferromagnetic component in the \( ab \)-plane. The field dependence is similar to CePdGa₆ [3] where the magnetization shows a jump at 2 T, lower than the metamagnetic transition of Ce₂PdGa₁₂.

### 3.3. Specific heat

As discussed in the synthesis section, we have established synthetic routes to obtain single-phase crystals for both CePdGa₆ and Ce₂PdGa₁₂. Their temperature dependences of the specific heat were measured and are shown in Fig. 6.
Two distinct Ce–Ce distances represent the structure of both compounds: Ce–Ce distances along the \(ab\)-plane, \((\text{Ce–Ce})_{ab}\), and \(c\)-axis, \((\text{Ce–Ce})_c\). In CePdGa\(_6\), the Ce–Ce interatomic distances are 4.350(3) Å in the \(ab\)-plane and 7.922(6) Å along the \(c\)-axis [3]. As for Ce\(_2\)PdGa\(_{12}\), since Ce atoms separate PdGa\(_8/2\) and Ga-only segments that stack along the \(c\)-axis, there are two distinct (Ce–Ce) distances along the \(c\)-axis. Thus, the \((\text{Ce–Ce})_{ab}\) interatomic spacing in Ce\(_2\)PdGa\(_{12}\) is 4.318(6) Å and \((\text{Ce–Ce})_c\) distances measure 7.664(5) Å and 7.882(6) Å. For both compounds, one would expect the magnetic correlations in the \(ab\)-plane to be stronger than those along the \(c\)-axis.

Coupled with the comparable crystal structures and the similar Ce–Ce distances found in both compounds, CePdGa\(_6\) and Ce\(_2\)PdGa\(_{12}\) are expected to share similar overall physical properties, that is, an antiferromagnetic ground state and metamagnetic transition under a field applied along the \(c\)-axis. On the other hand, there are still some differences between the two. The higher Néel temperature with ferromagnetic component and the smaller \(\gamma\) for Ce\(_2\)PdGa\(_{12}\) may result from the difference of the number of Pd in the unit cell.

Ce–Ce distances are longer than the Hill limit, suggesting that Ce \(f\) moments interact through RKKY (Ruderman–Kittel–Kasuya–Yosida) interactions by hybridizing with conduction electrons of surrounding Ga atoms. Hybridization also induces the Kondo effect that should suppress the Néel order by competing with RKKY interactions. Reduced entropy \((S\sim 5000 \text{ mJ/mole-K})\) at \(T_N\) in CePdGa\(_6\) suggests that the Kondo effect is more pronounced in CePdGa\(_6\) suppressing \(T_N\) further in comparison with Ce\(_2\)PdGa\(_{12}\). However, the difference in the Ce–Ga hybridization should not be the main reason for the differences between the two compounds because the Ce–Ga interatomic distances are nearly the same for both compounds. Hence, it is likely that the Pd atoms affect the magnetic properties by providing carriers to the systems. Ce\(_2\)PdGa\(_{12}\) has one less Pd atom than “Ce\(_2\)PdGa\(_{12}\)” (obtained by doubling the chemical formula of CePdGa\(_6\)). Generally, the decrease in the carrier number should result in two effects: (1) more localized nature of \(4f\) electrons because of lack of screening by conducting carriers, and (2) proximity to the ferromagnetic state through RKKY interactions.
The observed weaker Kondo effects along with ferromagnetic components in Ce$_2$PdGa$_{12}$ are indeed consistent with the smaller number of carriers due to less Pd in comparison with CePdGa$_6$.

4. Conclusion

We have synthesized Ce$_2$PdGa$_{12}$, which has a structure closely related to CePdGa$_6$. Our magnetic and thermal measurements have revealed double magnetic transitions. An antiferromagnetic transition occurs at 11 K, while a ferromagnetic component in the $ab$-plane appears by means of a second transition at $\sim$5 K. This metamagnetic transition is most likely due to a spin flop interaction. Comparing the structures and magnetic behavior with those for CePdGa$_6$, we argue that the $f$-electron state of Ce$_2$PdGa$_{12}$ is more localized and close to a ferromagnetic state because the carrier density is decreased by the lack of Pd atoms. It would be interesting to further study the effects of layering and Pd carriers by synthesizing a compound such as “Ce$_3$PdGa$_{18}$”. This insertion of Ga layers between each ‘CePdGa$_6$ layer’ may allow us to tune the transition temperature further.

**Crystallographic Information Available:** Crystallographic information files are available for La$_2$PdGa$_{12}$ and Ce$_2$PdGa$_{12}$.

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