Pr_{1.33}Pt₄Ga₁₀: Superstructure and Magnetism

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Abstract

$\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ crystals were prepared by Ga-flux method. The superstructure of this compound was studied by single-crystal X-ray diffraction (XRD), transmission electron microscopy (TEM), and diffuse X-ray scattering. $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ adopts the $P6_3/mmc$ space group with $a = b = 4.3227(5)$ Å, $c = 16.485(3)$ Å: the structure features Pr_2Ga_3 layers alternating with Pt_2Ga_4 layers along the c -axis. TEM studies and pair distribution function (PDF) analysis of X-ray total scattering data show that Pr_2Ga_3 layers possess an ordered superstructure (of dimension $a' = a\sqrt{3}$) in which Pr vacancies and Ga atoms are ordered within the ab -plane but disordered along the c -direction. PDF analysis also shows temperature-dependent structural features local to the Pr^{3+} ion. Magnetic measurements reveal that Pr^{3+} ions order ferrimagnetically below 12.5(2) K.

Keywords: $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$, superstructure, intermetallic, pair distribution function, transmission electron microscopy, magnetism

1. Introduction

Intermetallic compounds containing *f*-elements are among the most active research topics in the exploratory synthesis of correlated electron materials. Among them stands out a class of compounds known as heavy-fermions where strong hybridization between conduction electrons and *f*-electrons generates quasiparticles with effective masses several order of magnitudes larger than that of a free electron. This behavior results in a very large Sommerfeld coefficient of specific heat, γ , typically ≥ 400 mJ/(mol K²). The instability of localized *f*-electrons under chemical doping, high pressure, and applied magnetic field also contributes to interplay of physical properties of these materials, such as superconductivity and magnetism [1].

Layered structures are a common characteristic of many superconducting materials, and theoretical calculations show that the magnetic pairing is more robust in quasi two-dimensional structures than in three-dimensional structures [2,3]. Therefore, the synthesis of new rare-earth intermetallic compounds with layered structures has attracted attention in the area of heavy-fermion superconductors. In this respect, ternary transition metal rare-earth intermetallics with high content of *tri*el elements (Al, Ga, In) are especially appealing because they exhibit a variety of layered structures. For example, the tetragonal crystal structure of Ce_nMIn_{3n+2} (M = Co, Ir, Rh) can be viewed in terms of *n*-fold layers of CeIn₃ separated by layers of MIn₂ [4]. CeCoIn₅ and CeIrIn₅ (*n* = 1) are superconducting at 2.3 and 0.4 K, respectively, while Ce₂RhIn₈ (*n* = 2) becomes superconducting at 2 K under pressure of 25 kbar [5-7].

Many ternary compounds of the general composition Ln_xT_yX_z (Ln = lanthanide, T = transition metal and X = Al, Ga) with a high X content possess layered *ABAB* structures [3,8-15]. Typically, the *A* layer consists of Ln and X metals, and the *B* layer consists of T and X metals. For example,

in $\text{Er}_4\text{Pt}_9\text{Al}_{24}$, $\text{Y}_2\text{Co}_3\text{Ga}_9$, and $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$, *A* and *B* layers have the composition Er_2Al_3 , Y_2Ga_3 , Ce_2Ga_3 and PtAl_2 , CoGa_2 , Pt_2Ga_4 , respectively.

$\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$ consists of hexagonal Ce_2Ga_3 layers alternating with Pt_2Ga_4 layers along the crystallographic *c*-axis. It belongs to a series $\text{Ln}_{2-x}\text{Pt}_4\text{Ga}_{8+y}$ ($x \approx 0.66$, $y \approx 2.0$; $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd, Er, Yb, and Y}$), which was first reported by Lacerda et al [13]. $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$ is a heavy-fermion compound that does not exhibit any signs of magnetic ordering down to 2 K [13,16]. $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$, on the other hand, exhibits a low-temperature, field-dependent magnetic transition [13]. We have successfully grown large representative single crystals of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ and characterized the local structure and physical properties. Single crystal X-ray diffraction (XRD), transmission electron microscopy (TEM), and atomic pair distribution function (PDF) analysis have been used to provide, for the first time, a detailed description of the structural disorder observed in this compound. In addition, magnetic measurements confirm the results obtained earlier by Lacerda et al. and demonstrate significant magnetic anisotropy of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$.

2. Materials and Methods

2.1 Synthesis. Single crystals of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ were prepared using Ga-flux. A mixture of 0.327 g Pr (2.32 mmol), 0.343 g Pt (1.77 mmol), and 2.47 g Ga (35.4 mmol) was placed in an alumina crucible. The crucible and its contents were sealed under vacuum in a fused silica ampoule, and then heated to 1150 °C in the box furnace for 4 h before cooling down to 350 °C at a rate of 8 °C/h. The ampoule was removed from the furnace at 350 °C and immediately inverted and placed into a centrifuge. The excess liquid Ga was removed by centrifugation of the inverted ampoule for 10 min. The product contained hexagonal rod crystals of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ ($\approx 10\%$ yield with respect to Pr). The residual Ga flux remaining on the $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ crystal surface was removed by placing the crystals in a 3M solution of I_2 in DMF. Crystals of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ are stable in air for

several months. Wavelength-dispersive microprobe analysis of multiple crystals resulted in a chemical formula of $\text{Pr}_{1.508(6)}\text{Pt}_{3.8(1)}\text{Ga}_{10.0(1)}$, which is in agreement with single-crystal XRD results.

2.2 Single crystal X-ray diffraction. A fragment (approximately 0.01 mm x 0.01 mm x 0.03 mm) cut from a larger single crystal was mounted onto the goniometer of a Bruker KappaCCD diffractometer equipped with $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Data collection and structure solution were performed with SIR97 [17]. Structural refinements and extinction corrections were performed using SHELXL suite [18]. Further crystallographic details are included in Table 1; atomic positions and displacement parameters are provided in Table 2. Select interatomic distances are listed in Table 3.

Transmission electron microscopy and electron diffraction. TEM analysis was carried out on a probe aberration corrected sub- $\text{\AA}$ resolution JEOL JEM-ARM200cF microscope operated at 200 kV. The TEM sample was prepared by crushing a small piece of a single crystal with a mortar and pestle in methanol, and dropping the suspension onto a carbon/formvar coated 200 mesh Cu TEM grid. The TEM data was obtained from selected thin electron transparent single crystal pieces. Atomic resolution images along the major axis were obtained using scanning transmission electron microscopy high angle annular dark field imaging techniques (STEM HAADF). STEM images were taken with the JEOL HAADF detector using the following experimental conditions: probe size 7c, CL aperture 30 μm , scan speed 32 $\mu\text{s}/\text{pixel}$, and camera length 8 cm. The STEM resolution of the microscope is 0.78 $\text{\AA}$. The inner detector collection angle is 76 mrad. Electron diffraction patterns were obtained by tilting the crystal pieces to align along the major axis.

Table 1. Crystallographic data for Pr_{1.33}Pt₄Ga₁₀

Formula	Pr _{1.33} Pt ₄ Ga ₁₀
Space group	<i>P6₃/mmc</i> (No.194)
Crystal system	Hexagonal
<i>a</i> = <i>b</i> (Å)	4.3227(5)
<i>c</i> (Å)	16.485(3)
<i>V</i> (Å ³)	266.77(7)
<i>Z</i>	1
FW (g/mol)	1672.8
ρ_{calcd} (g/cm ³)	10.413
<i>T</i> (K)	293(2)
λ (Å)	0.71073
Completeness to $\theta=25^\circ$	99.2%
θ_{maximum}	45.24
Number unique reflections	484
Number reflections $I > 2\sigma(I)$	430
Number of refined parameters	19
Extinction coefficient	0.0121(9)
μ (mm ⁻¹)	83.083
<i>R</i> (int)	0.0501
<i>R</i> (<i>F</i>) ^a	0.0332
<i>R_w</i> (<i>F_o</i> ²) ^b	0.0776
GOF (<i>F</i> ²) ^c	1.144
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$	-5.42, 7.23

$$^a R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$^b R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

$$^c \text{Goodness of fit (GoF)} = \{(\Sigma |w| |F_o^2 - F_c^2|) / (n - p)\}^{1/2} \text{ where } n$$

= number of reflections used and *p* = number of refined parameters

Table 2. Atomic coordinates and isotropic displacement parameters of Pr_{1.33}Pt₄Ga₁₀

Atom	Wyckoff site	x	y	z	Occupancy	$U_{eq} (\text{\AA}^2)^a$
Pr	$2d$	1/3	2/3	1/4	0.708(7)	0.005(1)
Pt	$4f$	2/3	1/3	0.10806(2)	1	0.007(1)
Ga(1)	$4e$	0	0	0.13682(9)	1	0.008(1)
Ga(2)	$2d$	1/3	2/3	0.04613(8)	1	0.008(1)
Ga(3)	$6h$	0.5348(5)	0.0696(9)	1/4	0.322(7)	0.007(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected interatomic distances (Å) for Pr_{1.33}Pt₄Ga₁₀

Atom Pair	Distance (Å)
Pt-Ga(1)	2.5405(4)
Pt-Ga(2)	2.541(1)
Pt-Ga(2)	2.6956(6)
Pt-Ga(3)	2.541(2)
Pt-Pr	3.4223(4)
Pr-Ga(1)	3.1166(9)
Pr-Ga(3)	3.109(3)
Ga(1)-Ga(2)	2.909(1)
Ga(2)-Ga(2)	2.923(1)
Ga(1)-Ga(3)	2.868(1)
Ga(3)-Ga(3)	2.613(6)

2.3 High energy X-ray total scattering measurement. A pulverized sample of Pr_{1.33}Pt₄Ga₁₀ was loaded in a polyimide capillary of 0.0435" outer diameter (Cole-Parmer EW-95820-09). The

X-rays (58.26 keV, 0.2128 Å) available at the 11-ID-B beamline at the Advanced Photon Source at Argonne National Laboratory were used to collect X-ray total scattering data, in the range of 80 - 298 K at regular 1.5 K intervals. Sample temperature was controlled using an Oxford Cryostream 700 plus. Raw images were reduced with Fit-2D [19].

2.4 Magnetization and resistivity. Magnetic measurements were performed on a polycrystalline or a single-crystal sample with a Quantum Design SQUID magnetometer MPMS-XL. Field-cooled (FC) and zero-field cooled (ZFC) magnetization measurements were carried out in an applied field of 0.100 T in the 1.8–300 K temperature range. Hysteresis was measured with the magnetic field varying from -7 to 7 T.

3. Results and Discussion

3.1 Crystal structure. $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ is isostructural with $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$ and $\text{Gd}_{1.33}\text{Pt}_4\text{Al}_{10}$. The material crystallizes in hexagonal space group $P6_3/mmc$ and contains five atoms in the asymmetric unit. Of these, Pt, Ga(1), and Ga(2) atoms are at fully occupied $4f$, $4e$, and $4f$ Wyckoff sites, respectively, and form a Pt_2Ga_4 double layer perpendicular to the c -axis. The other two atoms, Pr and Ga(3), are at partially occupied $2c$ and $6h$ Wyckoff sites with occupancies of 0.708(7) and 0.322(7), respectively. The Pr and Ga(3) atoms form a hexagonal Pr_2Ga_3 layer perpendicular to the c -axis. The Pt_2Ga_4 and Pr_2Ga_3 layers stack alternatively along the c -axis direction with an $ABAB\dots$ stacking sequence (Figure 1).

Figure 1. Ball-and-stick representation of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ shows Pt_2Ga_4 double layers and Pr_2Ga_3 layers along the c -axis. Interlayer Pr-Ga and Pt-Ga bonds between Pt_2Ga_4 double layers and Pr_2Ga_3 layers have been omitted for clarity. Blue, gray, and orange spheres represent Pr, Pt, and Ga atoms, respectively. Dashed lines outline the unit cell.

The Pt_2Ga_4 double layer can be constructed by positioning two PtGa_2 single layers parallel to each other and binding Ga(2) atoms of one layer to Pt atoms of the other layer along the c -axis (Figure 1). Each PtGa_2 single layer is comprised of a hexagonal net of Pt atoms sandwiched between a hexagonal net of Ga(1) atoms and a hexagonal net of Ga(2) atoms (Figure 2). Within the PtGa_2 layer, the Pt-Ga(1) and Pt-Ga(2) distances are 2.5405(4) Å and 2.6956(6), respectively, while the interlayer Pt-Ga(2) distances between two PtGa_2 layers are 2.541(1) Å, which are shorter than the intralayer Pt-Ga(2) distances.

Figure 2. Ball-and-stick representation of the PtGa_2 single layer (top) and an ordered structure of Pr_2Ga_3 (bottom). In the PtGa_2 single layer, Ga(2) atoms connected to Pt atoms represented by dash bonds whereas Pt-Ga(1) bonds are solid lines. In the Pr_2Ga_3 layer, orange triangles are $\text{Ga}(3)_3$ trimers centered inside Pr-hexagons, shown as blue spheres and dashed lines.

The Pr_2Ga_3 layers consists of partially occupied Pr and Ga(3) atoms with site occupancies of 0.708(7) and 0.322(7), respectively, which deviate slightly from the $2/3$ and $1/3$ values that are required to obtain the composition of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$. These deviations have been seen in other $\text{Ln}_{1.33}\text{Pt}_4\text{X}_{10}$ compounds ($\text{X} = \text{Al}, \text{Ga}$), where the occupancies of Ln and X sites have been observed to be as low as 0.5 and as high as 0.37, respectively [10,14,15,20,21]. These site occupancy deviations further contribute to the disorder of Ln_2X_3 layers and their superstructure. A fully-occupied rare-earth layer would result in a Pr_3Ga_9 stoichiometry and Pr-Ga(3) and Ga(3)-Ga(3) distances of 1.508(4) Å and 1.710(6) Å, respectively. However, these atomic distances are much shorter than sums of Pr (1.85 Å) and Ga (1.30 Å) atomic radii [22], which would lead to a chemically unreasonable structure. By removing approximately $1/3$ of Pr atoms and $2/3$ of Ga(3) atoms, as reflected by the experimental site occupancies, the composition of the layer changes to Pr_2Ga_3 , with reasonable Pr-Ga(3) and Ga(3)-Ga(3) distances of 3.109(3) Å and 2.613(6) Å, respectively. In this model, the coordination environment of the Pr site is represented by a penta-

capped trigonal prism (Figure 3). Six Ga(1) atoms form the trigonal prism while three Ga(3) atoms cap the three rectangular faces and 2 Ga(2) atoms cap the two trigonal faces.

Given the experimental site occupancies (obtained from single-crystal XRD) and the layered structure, the chemical formula of the title compound can be rewritten as $(\text{Pr}_{0.67}\text{Ga})_2(\text{Pt}_2\text{Ga}_4)_2$. The Pt-Pr, Pt-Ga(3), and Pr-Ga(1) distances between Pr_2Ga_3 layers and Pt_2Ga_4 double layers are 3.4223(4) Å, 2.541(2) Å, and 3.117(1) Å, respectively.

Figure 3. Polyhedral representations of Ga-coordination environments of Pr and Pt atoms. Blue, gray, and orange spheres represent Pr, Pt and Ga, respectively.

Disorder and superstructure of Ln_2X_3 layers. The disorder of Ln and X (Al, Ga) atoms and the superstructure of the Ln_2X_3 layer in compounds related to $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ have been extensively studied by X-ray and neutron diffraction. Interestingly, all these compounds contain Ln_2X_3 layers with hexagonal symmetry, but they crystallize in different crystal systems, including triclinic ($\text{Ln}_4\text{Pt}_9\text{Al}_{24}$) [11], orthorhombic ($\text{Y}_2\text{Co}_3\text{Ga}_9$) [23], trigonal (LnNi_3Al_9) [24], and hexagonal ($\text{Ln}_{1.33}\text{Pt}_4\text{Al}_{10}$) [15]. Besides trielides (X = Al, Ga), this layered structure is also found in transition-metal iron silicides, e.g., $\text{Sc}_{1.2}\text{Fe}_4\text{Si}_{9.9}$ which has been recently extended to $\text{Ln}_{2-x}\text{Fe}_4\text{Si}_{14}$.

y [25]. For compounds containing Al and Ga, there exists a consensus that the $\text{Ln}_2\text{Ga}(\text{Al})_3$ layer has a honeycomb superstructure of Ln atoms with Ga_3 (Al_3) triangles located in the center of each rare-earth hexagonal unit. Ga_3 triangles have also been recently observed in $\text{Sr}_2\text{Au}_6\text{Ga}_3$ [26]. Perhaps the most convincing evidence for ordered Ga_3 triangles in the title compound is that diffraction spots in the $[hk0]$ zone can be indexed to a larger supercell with dimensions of $a\sqrt{3} \times a\sqrt{3}$ [15,20,21]. Streaks extending along the reciprocal c^* -axis in single crystal X-ray and neutron diffraction patterns have been observed for $\text{Ln}_4\text{Pt}_9\text{Al}_{24}$, $\text{Ln}_{1.33}\text{Pt}_4\text{Al}_{10}$, and LnNi_3Al_9 , but the superstructure along the c -direction has yet to be determined because of the weak and diffuse nature of these streaks [11,15,24]. All these considerations incited us to further investigate the disorder and superstructure of Pr_2Ga_3 layers in $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ by TEM and PDF methods.

Figure 4. Pr and Ga(3) vacancies of ordered structure of Pr_2Ga_3 layers from the single crystal data and TEM data. Stacking of Pr_2Ga_3 layers along the c -axis contribute to the observed superstructure of Pr_2Ga_3 layers. Blue, gray, and orange spheres represent Pr, Pt and Ga, respectively, while red pentagons and red squares represent Pr and Ga(3) vacancies, respectively.

3.2 Transmission Electron Microscopy and Electron Diffraction. Atomic resolution STEM HAADF Z-contrast images and electron diffraction (ED) pattern of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ are provided in Figure 5. Figure 5a shows well-ordered diffraction spots in the $[1-100]$ zone direction. Two sharp streak lines observed in the ED pattern (labeled S1 and S2 in Figure 5a) have d -spacing values of 6.45 Å and 3.20 Å; their shape indicates disorder along the c axis. The origin of the diffraction streaks will be discussed later.

Figure 5. (a) ED pattern of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ along $[1-100]$; (b) Atomic resolution STEM HAADF Z-contrast image of the crystal projected down $[1-100]$ showing the ordering of Pr vacancies along $[11-20]$. (c) Enlarged image with Pr vacancies highlighted with white circles. (d) Higher magnification image showing Pt, Pr and Ga atoms. (e) FFT of (b); (f) Top: Experimental inverse FFT image; Middle: inverse FFT from the 6.45 Å diffraction streak, and the lower image is the inverse FFT from the 3.20 Å diffraction streak.

Intensities observed in STEM HAADF images are proportional to the atomic number Z^n (where n is close to 2).[27,28] Figure 5b is an atomic resolution STEM Z-contrast image of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ projected along the $[1-100]$ direction. Because of the large differences in Z of Pt, Pr, and Ga ($Z = 78, 59$, and 31 , respectively), the Pt atoms appear as the brightest intensity in the image while Pr atoms are observed as less intense rows sandwiched between the brighter Pt spots. Upon close inspection, it is obvious that the intensities of the Pr atoms vary such that for every two brighter

Pr spots, one darker Pr spot follows along the [11-20] direction. This pattern (of bright Pr/bright Pr/dark Pr) is shown in Figure 5c. In addition to dependence upon the atomic number, Z , atom intensities in STEM HAADF Z-contrast images also have a linear relationship with the number of atoms. Thus, these darker Pr spots correspond to Pr vacancies in that column.

The images show Ga(3) atoms with similar intensity as Ga(1) atoms beside Pr vacancies, and that there are no Ga(3) atoms between occupied Pr atoms. Figure 5d has a high magnification, which clearly shows each atom. The smaller atoms above and below the Pr vacancy are the Ga(3) atoms. The bottom inset shows that not all Pr vacancy positions are aligned along the c -axis, rather, they are shifted relative to the adjacent ab -plane. Each Pr vacancy in the [1-100] direction is separated by two occupied Pr sites, which is consistent with the occupancy of 0.708(7) obtained from single-crystal XRD.

The fast Fourier transformation (FFT) of Figure 5b is shown in Figure 5e. The two sharp diffraction streaks show up in the FFT image, the same as those observed in the ED pattern. The inverse FFT images obtained from each of the streak features are shown in Figure 5f, where the top image is the original experimental image, the middle image is the inverse FFT from the 6.45 Å diffraction streak, and the lower image is the inverse FFT from the 3.20 Å diffraction streak. These three images are aligned to show that the periodicities in intensities derive from the Pr/Ga(3) columns.

The pattern of black and white intensities in the inverse FFT image from streak 1 reveals that the periodicity of Pr-vacancies is 6.45 Å, which agrees well with the calculated distance of 6.48 Å between two Pr-vacancy lines in the Pr₂Ga₃ layer, confirming the ordering of the Pr-vacancies within each layer. However, Pr-vacancies are not ordered along the c axis, as the positions of the Pr-vacancies are shifted within the ab -plane with respect to an adjacent Pr₂Ga₃ layer. This

observation agrees with the previous studies on stacking of Ln_2X_3 layers in $\text{Ln}_4\text{Pt}_9\text{Al}_{24}$, $\text{Ln}_{1.33}\text{Pt}_4\text{Al}_{10}$, and $\text{Gd}_{1.33}\text{Pt}_4\text{Ga}_{10}$ [11,15,20], as well as with the superstructure model of the Pr_2Ga_3 layer obtained from single-crystal XRD (Figure 4). According to the single-crystal XRD model, the distances between Ga(3)-vacancy columns and Pr-vacancy columns is one-half of the periodicity of Pr-vacancy columns (3.24 Å), which is consistent with the periodicity of vacancies in the inverse FFT image from streak 2 (3.2 Å) along the [1-100] direction.

3.3 Pair distribution function analysis. PDF analysis was based on variable temperature X-ray total scattering data collected at beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. Our initial model was based on the crystal structure obtained from single-crystal XRD experiments. In refinements using PDFGUI, the lattice parameters, atomic positions, and isotropic thermal parameters of all atoms were allowed to refine while keeping site occupancies of all atoms fixed. No structural transitions were observed for $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ between 80 and 298 K. Weighted R_w for refinements performed in PDFGUI range between 25.4% and 20.7% for all data between 80 to 298 K. Figure 6a shows a good fit between the experimental PDF data and the calculated PDF (from the single-crystal XRD) model, indicating that the structural model of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ obtained from single crystal XRD fairly describes the local crystal structure. However, there is one peak at ~ 3.2 Å that is not described well by the single-crystal XRD model. The local structure associated with this peak will be discussed in further detail.

The partial PDFs of each atomic pair (which were calculated from the single-crystal model) and observed and calculated $G(r)$ plots in the range $2 < r < 4.0$ Å are presented in Figure 6b. The highest residual peak, which occurs at ~ 3.2 Å, corresponds to neither the 3.4223(4) Å Pr-Pt distance nor the ~ 3.11 Å Pr-Ga distances determined from single-crystal XRD. This mismatch

can be easily visualized in Figure 6b where all peaks in the $G(r)$, except for the peak at ~ 3.2 Å, can be assigned to interatomic pairs based on calculated partial PDFs.

None of the atomic displacement parameters from single-crystal diffraction were significantly elongated; however, to assess the possibility that the peak in the residual at 3.2 Å reflected disorder in the Ga position, a single-crystal refinement with a split-Ga(1) site was attempted. The Ga(1) site was chosen for further investigation for two reasons. In the original single-crystal XRD refinement, the Ga(1) site had the least spherical thermal ellipsoid. In addition, the largest Q-peak in our original single-crystal XRD refinements corresponded to a Pr-Ga distance of ~ 3.2 Å. The refinement of the split Ga(1) model proved to be worse than the original model; R_{wp} (= 0.0349) for the split Ga(1) model did not improve and the thermal ellipsoid of the newly formed Ga site became unusually oblong ($U_{11} = 0.00840$, $U_{22} = U_{33} = 0.00376$). Therefore, disorder of the Ga site is not a reasonable explanation for the ~ 3.2 Å peak in the PDF data.

Another interesting observation was made in the temperature-dependent PDF data shown in Figure 6c. With increasing temperature, the Pr-Ga vacancy peak shifts to larger r ; this peak clearly broadens and shifts from $\sim 3.16(1)$ Å at 80 K to $\sim 3.20(1)$ Å at 298 K. The Pr-Pt peak also broadens but continuously shifts with increasing temperature to smaller r until it reaches $\sim 3.38(1)$ Å by 298 K. These peak positions were obtained from fitting the first four peaks of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ PDF data using Gaussian peak shape functions.[29] Neither the Pt-Ga nor the Ga-Ga peak shifts with temperature (besides a slight increase due to thermal motion). These opposing trends in the Pr-Ga vacancy and Pr-Pt peaks may be the result of the Pr and Ga(3) vacancies, for which evidence was observed in TEM data. Vacancy ordering in intermetallics can result in a supercell and hence, be observed via X-ray diffraction. Recent examples of such experimental evidence have been observed for $\beta\text{-Fe}_{1-x}\text{Se}$ [30], SmGe_{2-x} [31], and type-I clathrate, $\text{Rb}_8\text{Sn}_{44}\square_2$

intermetallics ($\square$ = vacancy) [32]. Fässler et al. proposed a model of local structural relaxation for ordered vacancies in $\text{Rb}_8\text{Sn}_{44}\square_2$ where Sn- $\square$ distances are shorter than typical Sn-Sn bonds and nearest-neighbor Sn-Sn contacts are elongated to compensate for the vacancies. We postulate that a similar local structural relaxation due to the Pr and Ga(3) vacancies can be observed in PDF data. This is most clearly seen at 80 K where the Pr-Ga vacancy distance is at its shortest (at 3.16(1) Å) while the Pr-Pt distance is at its longest (at $\sim$ 3.40(1) Å).

It should also be noted that analogous Ce-Ga and Ce-Pt peaks show no temperature dependence within the same temperature range of 80-298 K. Temperature-dependent $G(r)$ plots for $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$ are provided in Supplementary Information. Since $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$ does not exhibit magnetic ordering[33] in contrast to the ferrimagnetism of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$, it would be interesting to learn how the local structural environment around the Ln^{3+} ion influences the magnetic behavior. Because current cooling capabilities were limited to 80 K, PDF data could not be used to correlate the ferrimagnetic transition in $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ with the local environment, but we do not exclude the possibilities of such studies in the future.

Figure 6. Figure 6a compares experimental PDF data with the structural model derived from single crystal X-ray diffraction. Inset: Feature at $3.2 \text{ \AA}$ that does not agree with the single-crystal model. Figure 6b compares calculated partial PDFs of Ga-Pt, Ga-Ga, Pr-Ga, and Pr-Pt with experimental PDF data. Figure 6c shows temperature-dependent PDF data of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$.

3.4 Magnetism. Figure 7 shows the magnetization of a microcrystalline powder sample of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ as a function of temperature. A Curie-Weiss fit to the linear part of the temperature-dependent portion of the data gives a Weiss constant $\theta = -20.8$ K, which indicates nearest-neighbor antiferromagnetic correlations. The Curie constant was determined to be 6.99 emu·K/mol per formula unit, which corresponds to an effective moment of $3.74 \mu_B$ per Pr atom. This value is close to the expected value of $3.58 \mu_B$ for a Pr^{3+} ion, indicating nearly a free-ion behavior at moderate temperatures. Upon cooling, the magnetization curve increases rapidly around 15 K and saturates below 8 K. This observation, along with the negative value of the Weiss constant, suggests $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ behaves as a weak ferromagnet (canted antiferromagnet). The antiferromagnetic coupling can be suppressed by applied magnetic field; as shown by field-dependent magnetization measurements (Figure 8), a metamagnetic transition takes place at $H \sim 2$ T. This findings agrees with the earlier observations by Lacerda et al [13]. At 7 T, the magnetization saturates at $\sim 1.5 \mu_B$ per Pr^{3+} ion, which is much lower than the theoretical expectation value of $3.20 \mu_B$. Thus, a significant antiferromagnetic exchange component is still present at 7 T, the highest field available in our experiment, suggesting that another metamagnetic transition to a ferromagnetically ordered state might be possible at higher fields.

The magnetic behavior was also studied on an oriented single crystal of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$. The measurements of the field-cooled (FC) and zero-field-cooled (ZFC) magnetic response revealed a significantly higher magnetization value when the applied magnetic field was parallel to the c axis (Figure 9), indicating the preferred alignment of the Pr moments in this direction. At both field orientations, the divergence of the FC and ZFC curves was observed at $T_C = 12.5(2)$ K, the temperature of magnetic phase transition.

Figure 7. Temperature dependence of FC (red circles) and ZFC (black circles) magnetization measured on a polycrystalline sample of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ in an applied field of 0.100 T. Inset: Temperature dependence of inverse magnetic susceptibility. The red line corresponds to the Curie-Weiss fit.

Figure 8. Hysteresis curve measured on a polycrystalline sample of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ at 1.8 K. Inset: The magnified (low-field) section of the plot.

Figure 9. Temperature dependence of FC (closed symbols) and ZFC (open symbols) magnetization measured under applied field parallel of 0.100 T (red circles) and perpendicular (black triangles) to crystallographic c -axis on single crystals of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$.

Conclusion

The structural properties of $\text{Pr}_{1.33}\text{Pt}_4\text{Ga}_{10}$ have been analyzed using single-crystal X-ray diffraction, TEM, and PDF analysis. Single-crystal X-ray diffraction and TEM results support a superstructure model with partially occupied ($\sim 2/3$) Pr sites. The periodicity of the Pr-vacancies measures 6.45 Å and confirms that Pr vacancies occur within the plane and not along the c -axis. The PDF analysis showed that the single crystal model provided a generally good fit with experimental data. A peak at ~ 3.20 Å was observed, but not yet explained. Temperature-dependent PDF data show that Pr-Pt distances increase with temperature, but that Pr-Ga distances decrease with temperature. These trends may suggest structural relaxation about the Pr and Ga3 vacancies.

Magnetization studies show that the Pr^{3+} ion exhibits a metamagnetic transition at ~ 2 T and that studies regarding a possible second metamagnetic transition to a ferromagnetic state occurs with applied fields greater than 7 T. These studies are currently underway in our laboratories.

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