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$Pr_{1.33}Pt_4Ga_{10}$: Superstructure and magnetism

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ABSTRACT

$Pr_{1.33}Pt_4Ga_{10}$ 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. $Pr_{1.33}Pt_4Ga_{10}$ 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.

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 K^2). 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 *triel* 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 $CeIn_3$ separated by layers of MIn_2 [4]. $CeCoIn_5$ and $CeIrIn_5$ ($n=1$) are superconducting at 2.3 K and 0.4 K, respectively, while Ce_2RhIn_8 ($n=2$) 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 $Er_4Pt_9Al_{24}$, $Y_2Co_3Ga_9$, and $Ce_{1.33}Pt_4Ga_{10}$, *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.

$Ce_{1.33}Pt_4Ga_{10}$ consists of hexagonal Ce_2Ga_3 layers alternating with Pt_2Ga_4 layers along the crystallographic *c*-axis. It belongs to a series $Ln_{2-x}Pt_4Ga_{8+y}$ ($x \approx 0.66$, $y \approx 2.0$; Ln=La, Ce, Pr, Nd, Sm, Gd, Er, Yb, and Y), which was first reported by Lacerda et al. [13]. $Ce_{1.33}Pt_4Ga_{10}$ is a heavy-fermion compound that does not exhibit any signs of magnetic ordering down to 2 K [13,16]. $Pr_{1.33}Pt_4Ga_{10}$, on the other hand, exhibits a low-temperature, field-dependent magnetic transition [13]. We have successfully grown large representative single crystals of $Pr_{1.33}Pt_4Ga_{10}$ 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

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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 $Pr_{1.33}Pt_4Ga_{10}$.

2. Materials and methods

2.1. Synthesis

Single crystals of $Pr_{1.33}Pt_4Ga_{10}$ 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 $Pr_{1.33}Pt_4Ga_{10}$ (≈10% yield with respect to Pr). The residual Ga flux remaining on the $Pr_{1.33}Pt_4Ga_{10}$ crystal surface was removed by placing the crystals in a 3 M solution of I_2 in DMF. Crystals of $Pr_{1.33}Pt_4Ga_{10}$ are stable in air for several months. Wavelength-dispersive microprobe analysis of multiple crystals resulted in a chemical formula of $Pr_{1.508(6)}Pt_{3.8(1)}Ga_{10.0(1)}$, which is in agreement with single-crystal XRD results.

2.2. Single crystal X-ray diffraction

A fragment (approximately 0.01 mm × 0.01 mm × 0.03 mm) cut from a larger single crystal was mounted onto the goniometer of a Bruker KappaCCD diffractometer equipped with Mo$K\alpha$ (λ=0.71073 Å) 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.

2.2.1. Transmission electron microscopy and electron diffraction

TEM analysis was carried out on a probe aberration corrected sub-Å 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 μs/pixel, and camera length 8 cm. The STEM resolution of the microscope is 0.78 Å. The inner detector collection angle is 76 mrad. Electron diffraction patterns were obtained by tilting the crystal pieces to align along the major axis.

2.3. High energy X-ray total scattering measurement

A pulverized sample of $Pr_{1.33}Pt_4Ga_{10}$ 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].

Table 1
Crystallographic data for $Pr_{1.33}Pt_4Ga_{10}$.

Formula	$Pr_{1.33}Pt_4Ga_{10}$
Space group	$P6_3/mmc$ (No. 194)
Crystal system	Hexagonal
$a=b$ (Å)	4.3227(5)
c (Å)	16.485(3)
V (Å^3)	266.77(7)
Z	1
FW (g/mol)	1672.8
ρ_{calcd} (g/cm^3)	10.413
T (K)	293(2)
λ (Å)	0.71073
Completeness to θ=25°	99.2%
$\theta_{maximum}$	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
R(int)	0.0501
$R(F)$[a]	0.0332
$R_w(F_o^2)$[b]	0.0776
GOF (F^2)[c]	1.144
$\Delta\rho_{min}$, $\Delta\rho_{max}$	−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] Goodness of fit (GOF)=$\{(\sum|w/|F_o^2-F_c^2|^2|)/(n-p)\}^{1/2}$ where n=number of reflections used and p=number of refined parameters.

Table 2
Atomic coordinates and isotropic displacement parameters of $Pr_{1.33}Pt_4Ga_{10}$.

Atom	Wyckoff site	x	y	z	Occupancy	U_{eq} (Å^2)[a]
Pr	2*d*	1/3	2/3	1/4	0.708(7)	0.005(1)
Pt	4*f*	2/3	1/3	0.10806(2)	1	0.007(1)
Ga(1)	4*e*	0	0	0.13682(9)	1	0.008(1)
Ga(2)	2*d*	1/3	2/3	0.04613(8)	1	0.008(1)
Ga(3)	6*h*	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 $Pr_{1.33}Pt_4Ga_{10}$.

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)

2.4. 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.