Journal of Alloys and Compounds 600 (2014) 193–198

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Synthesis, structure, and magnetic behavior of $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$

Robin T. Macaluso [a,*], Michael Shatruk [b], Ping Chai [b], Hanyul Hong [a], Chad Wangeline [a], Kevin Ryan [a], Peter Holton [a], Julien Allaz [c], Gregory Morrison [d], Bradford Fulfer [d], Frank Fronczek [d], Julia Y. Chan [d,e]

[a] Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, CO 80639, United States
[b] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States
[c] Department of Geological Sciences, University of Colorado-Boulder, Boulder, CO 80309, United States
[d] Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States
[e] Department of Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States

ARTICLE INFO

Article history:
Received 14 December 2013
Received in revised form 14 February 2014
Accepted 17 February 2014
Available online 26 February 2014

Keywords:
Magnetic measurements
Single-crystal X-ray diffraction
Scanning electron microscopy
Crystal growth
Intermetallics
Rare earth alloys and compounds

ABSTRACT

$(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$, synthesized with excess Ga flux, crystallize in the $P6_3/mmc$ space group, $Z = 1$, with lattice parameters $a = b \sim 4.3$ and $c \sim 16.5$ Å for the entire range of the solid solution. Single-crystal diffraction and electron microscopy methods show that La substitution within the solid solution does not lead to systematic decrease in unit cell dimensions. The crystal structure of $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$ can be viewed as a combination of RE_2Ga_3 (*A*) and double Pt_2Ga_4 (*B*) layers stacked along the *c* axis in an *ABAB* sequence. $Ce_{1.33}Pt_4Ga_{10}$ exhibits a large negative Weiss constant, $\theta_W = -87.2$ K, but does not reveal any signature of magnetic ordering. An examination of zero-field-cooled and field-cooled magnetization curves and AC susceptibility at low temperatures excludes a possible formation of spin-glass state down to 1.8 K. These findings support an earlier suggestion that $Ce_{1.33}Pt_4Ga_{10}$ might exhibit non-Fermi liquid behavior.

1. Introduction

Short-range magnetic correlations in materials with frustrated or disordered arrangement of magnetic moments represent an exciting area of research. The existence of multiple magnetic ground states in such systems leads to interesting quantum phenomena, such as spin frustration, spin glass, and spin-liquid behavior [1–3].

Of particular interest is a growing class of RE/T/M (RE = rare-earth, T = transition metal, and M = Al, Ga, Si or Ge) intermetallics, in which magnetic anisotropy of RE is overlaid on the triangular geometry of RE-M layers. Inherently frustrated interactions between magnetically anisotropic centers can lead to unconventional magnetic behavior. For example, $Yb_2Pt_6Al_{15}$ exhibits a heavy Fermi liquid ground state and a local Yb^{3+} moment degeneracy [4]. On the other hand, $RE_2Pt_9Ge_3$ (RE = Y, Tb–Yb) [5] and $Gd_{1.33}Pt(Al, Si)_8$ [6,7] exhibit antiferromagnetic behavior. Examples of gallide compounds that exhibit spin glass behavior include $Ln_2Ag_{1-x}Ga_{10-y}$ and β-$LnNi_{0.91}Ga_4$ (Ln = Tb, Dy, Ho, Er) [8,9].

Theoretical calculations have shown that low-dimensional lattices of square, triangular, and honeycomb geometries with Heisenberg spins are strong candidates for exotic quantum critical points – where a 0 K phase transition is driven only by quantum fluctuations [10-12]. For materials with honeycomb lattices, next-nearest neighbor interactions can result in competing electronic ground states and unconventional behavior [13,14]. Examples of honeycomb lattices with interesting quantum behavior include $Bi_3Mn_4O_{12}$ [15], $Na_3Cu_2SbO_6$ [16,17], $InCu_{2/3}V_{1/3}O_3$ [18-20], and β-$Cu_2V_2O_7$ [21]. The possibility of strong magnetic frustration becomes especially pronounced in honeycomb lattices with 4f moments coupled through Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions, where the strength of magnetic exchange shows oscillatory dependence on the interatomic separations. Our interests in low-dimensional quantum critical behavior motivated us to grow single crystals of $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$. The parent intermetallic, $Ce_{1.33}Pt_4Ga_{10}$, exhibits superstructure due to ordering of vacancies in the Ce–Ga layer that is perpendicular to the *c*-axis [22,23]. This superstructure model includes ~2/3 occupancy of the 2c site by Ce and ~1/3 occupancy of the 6h site by Ga. To better reflect the partial occupancies of Ce and Ga, we refer to this material as $Ce_{1.33}Pt_4Ga_{10}$, which belongs to the $Sc_{1.2}Fe_4Si_{9.8}$ structure type [24]. Reflections along the c^* axis

* Corresponding author.
E-mail address: robin.macaluso@unco.edu (R.T. Macaluso).

http://dx.doi.org/10.1016/j.jallcom.2014.02.095
0925-8388/

were also observed for $Ce_{1.33}Pt_4Ga_{10}$, but their weak and diffuse nature prohibited the determination of a superstructure along the [00*l*] direction. Heat capacity measurements by Lacerda et al. revealed an exceptionally large Sommerfeld specific heat coefficient, $\gamma \approx 4$ J/mol K^2 [22]. In addition, this material exhibits classical experimental features of non Fermi-liquid (NFL) behavior, namely $-\log T$ dependence in magnetic susceptibility and specific heat for $T < 10$ K [25].

The suppression of long-range magnetic order in NFL as temperature approaches 0 K makes them ideal candidates in which to study quantum critical phenomena where the boundary between long-range and short-range magnetic behavior can be controlled with parameters such as pressure, chemical composition, or magnetic field. NFL materials on the verge of magnetic order are also ideal for investigations of structure–property relationships as they relate to an infinitely small energy scale [26]. The unique crystal structure and physical behavior motivated us to investigate the synthesis and structure–property relationships of solid solution $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$.

In this contribution, we report the growth of $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$ single crystals and explore how the partial substitution of La for Ce influences the structural and magnetic properties of this material. Our magnetic studies also lend support to the existence of NFL state for the honeycomb lattice of 4f magnetic moments in $Ce_{1.33}Pt_4Ga_{10}$.

2. Materials and methods

2.1. Synthesis

Single crystals of $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$ were grown from Ga flux. Starting materials for the preparation of the samples were in elemental form. Lanthanum and cerium rods (99.9%) were cut to pieces and weighed inside a N_2-filled glove box. Platinum shot (99.9%) and gallium shot (99.999%) were used as is. In our initial attempts, Ce, La, Pt, and Ga were placed in a 2.5-mL alumina crucible in a 1.5-*x*:*x*:1:20 M ratio. The crucible and its contents were sealed in an evacuated fused quartz tube. The ampoule was heated to 1150 °C at a rate of 300 °C/h. After 7 h at 1150 °C, the ampoule was cooled to 350 °C at a rate of 8 °C/h. When the furnace temperature reached 350 °C, the ampoule was removed from the furnace and immediately inverted and centrifuged for at least 10 min to remove excess gallium flux. The resulting products consisted of hexagonal rod-shaped crystals and polycrystalline samples that formed in a plate-like habit. Typical crystal size ranged from ~0.2 to 2.5 mm. Relative ratios of the hexagonal-rod shaped crystals and polycrystalline samples varied with different initial concentrations of *x*. The lowest relative concentration of hexagonal-rod shaped crystals in the product was observed for $x = 0.75$. We estimate by visual inspection a ~10–20% yield of rod-shaped crystals.

The synthesis route was repeated with different Ce, La, Pt, and Ga molar ratios of 1.33-*x*:*x*:1:20. Crystals prepared with this modified molar ratio were also found with hexagonal habit, but were considerably larger. Crystal dimensions ranged from 10 to 70 mm in length. Product yield of the hexagonal rods improved slightly with the 1.33-*x* Ce:*x* La:1 Pt:20 Ga ratio.

For all syntheses, crystals were mechanically extracted and soaked in a 3*M* I_2/DMF (dimethylformamide) solution for at least one hour to remove residual gallium on the surface. The crystals were not observed to decompose in air. The plate-like polycrystalline samples were not explored in this work. Initial attempts to obtain elemental ratios of the plate-like samples by SEM methods resulted in various compositions from one batch to another. For instance, for $x = 0$ and $x = 1$, the average elemental molar ratios were 1.9 Ce:1.0 Pt:9.7 Ga and 1.1 La:1.0 Pt:5.2 Ga, respectively. Several batches of the hexagonal rod-shaped crystals were prepared, and structure determinations and physical property measurements produced similar results for all batches.

2.2. Single-crystal X-ray diffraction

Fragments ~0.01 mm × 0.01 mm × 0.01 mm were cut from larger single crystals and mounted onto the goniometer of a Bruker KappaCCD diffractometer equipped with MoKα ($\lambda = 0.71073$ Å) radiation. Structure solutions were performed with SIR97 [27]. Structural refinements and extinction corrections were performed using SHELXL suite [28].

Similar to previous reports, our diffraction experiments also revealed reflections along the [00*l*] direction at $h \pm 1/3$ and $k \pm 2/3$. Such observations suggest the existence of a superstructure, but the low intensity and diffuse nature of the reflections prevented successful refinements of a superstructure model.

In a single-crystal X-ray diffraction study of ternary aluminides, Niermann and Jeitschko successfully applied a model with an ordered distribution of the 2*c* (containing Y or Zr) and 6*h* sites (containing Al) [24]. This treatment results in a hexagonal superstructure with ideal formulae of $Y_{1.33}Pt_4Al_{10}$ and $Zr_{1.33}Pt_4Al_{10}$ ($Z = 1$) with space group $P6_3/mmc$ and lattice parameters, $a \sim 4.3$ and $c \sim 16.4$ Å. This superstructure has also been observed in $Gd_{1.33}Pt_3(Al, Si)_8$ and $RENi_3Al_9$ [7]. Because diffuse reflections in the [00*l*] direction are similar to those in $Y_{1.33}Pt_4Al_{10}$ [24], we applied the structural model of $Y_{1.33}Pt_4Al_{10}$ to diffraction data collected for $(La_xCe_{1-x})_{1.3}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$. Atomic positions, anisotropic displacement parameters, and occupancy factors of Ce (or La) and Ga were each refined individually prior to refining all together. Formulae obtained from X-ray diffraction for $(La_xCe_{1-x})_{1.3}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$ are close to the ideal composition of $RE_{1.33}Pt_4Ga_{10}$ (RE = La, Ce). The excellent fit between crystallographic models and experimental data resulted in low R_1, typically ~3% and small residual electron density. Crystallographic parameters are listed in Table 1, and atomic positions and other structural information are listed in Table 2. Selected interatomic distances and bond angles are given in Table 3. Detailed information for members of the $(La_xCe_{1-x})_{1.33}Pt_4Ga_{10}$ $(0 \leqslant x \leqslant 1)$ series are provided in Supplementary Information. Single-crystal X-ray diffraction experiments performed on multiple crystal fragments from separate crystal-growth batches achieved similar results.

2.3. Electron microscopy

Semi-quantitative elemental analyses (without standards) were performed on several samples from each crystal-growth batch. Samples were placed under vacuum in a JEOL JSM-6610LV scanning electron microscope equipped with an Oxford XMac energy-dispersive X-ray (EDX) spectrometer. Single crystals were analyzed under 20 keV accelerating voltage and 180 s accumulation time. Multiple spots on clean surfaces of several crystals within a batch were analyzed to obtain an average composition.

Quantitative analyses of crystals were performed with a JEOL-8600 microprobe to determine composition. Crystals were mounted in epoxy resin and polished with a 1-μm diamond slurry. Crystal surfaces were coated with carbon prior to analysis. An electron beam was produced with an accelerating voltage of 15 kV and current of 50 nA and was focused to 1 μm. GaAs (Ga Lα on thallium acid phthalate, TAP, crystal), Pt metal (Pt Mα on pentaerythritol, PET, crystal), $CePO_4$ (Ce Lα on LiF crystal), and $LaPO_4$ (La Lα on LiF crystal) standards were analyzed prior to obtain precise quantitative results. The mean compositions are listed in Table 4.

2.4. Magnetic measurements

Magnetic measurements were performed on microcrystalline powders and on single crystals with a Quantum Design SQUID magnetometer MPMS-XL. DC magnetic susceptibility was measured in an applied field of 1–100 mT. The AC susceptibility was measured in zero DC bias field, with the AC field amplitude of 0.5 mT and frequency varying from 1 to 1000 Hz. Field-dependent magnetization data were collected at 1.8 K with the applied field varying from 0 to 70 kOe

Table 1
Crystallographic parameters of $La_{1.36(2)}Pt_{4.00(2)}Ga_{9.914(8)}$.

Experimental formula (XRD)	$La_{1.362(8)}Pt_{4.00(2)}Ga_{9.914(8)}$
$a = b$ (Å)	4.3424(1)
c (Å)	16.5973(7)
$\alpha = \beta$ (°)	90
γ (°)	120
V (Å^3)	271.04(2)
Z	1
T (K)	300(2)
ρ (calculated) (g cm^{-3})	10.180
Radiation (Å)	0.71073
$\Theta_{maximum}$ (°)	38.69
Collected reflections	168
Unique reflections, with $F_o^2 > 2\sigma(F_o^2)$	149
h	$-6 < h < 7$
k	$-7 < k < 6$
l	$-28 < l < 27$
No. of variables	18
$R(F)$ for F_o^2	0.0255
$R_w(F_o^2)$	0.0522
Extinction coefficient	0.0221(11)
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	−1.784, 2.224