Magnetic and thermodynamic properties of the $CeRhGa_4$ compound

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Abstract. $CeRhGa_4$ is reported in this work for the first time to crystallize in an orthorhombic structure having the $CeOsGa_4$ structure type belonging to the space group *Pmma*. The physical and magnetic properties of this compound were studied by specific heat $C_p(T)$, magnetization $M(\mu_0 H)$ and magnetic susceptibility $\chi(T)$. $\chi(T)$ and $C_p(T)$ results indicated that there is no magnetic transition above 2 K. The effective magnetic moment μ_{eff} obtained by fitting the Curie-Weiss law on the $\chi^{-1}(T)$ data is $\mu_{eff} = 2.32(3)\ \mu_B$, which is close to the theoretical value for a free Ce^{3+} ion. The negative value of the Weiss temperature, $\theta p = -40.562(4)$ K indicates that antiferromagnetic interactions at high temperatures are dominant. After $M(\mu_0 H)$ shows simple paramagnetic behaviour above 10 K, where M is linear in $\mu_0 H$ up to 20 K. The $C_p(T)/T$ increases sharply below 10 K to reach a very high value of 700 mJ/mol.K^2at 0.5 K. Future studies will focus upon the low temperature region to search for a possible magnetic phase transition.

1. Introduction

Ce-based intermetallic compounds have produced a huge amount of literature for the past four decades and still remain of great interest in the current research, depending on the valence state of Ce ion, see for example the published volume of international conference proceedings on Strongly Correlated Electron System 2017 [1]. The interaction between the single $4f$ electron of cerium and the conduction electrons of transition metals belonging to group 3, 4 and 5, produce fascinating behaviours, especially near the ground state at low temperatures [2]. The behaviours shown by these compounds include the Kondo behaviour observed in for example $CeRh_2Al_{10}$ [3], the noncentrosymmetric heavy fermion superconductor in $CeIrGe_3$ [4] and quantum criticality in $CeCu_2Si_2$ [5]. However, temperature is usually the driving force behind the valence state of the Ce ion, therefore it is for this reason why we observe such behaviours in these compounds. Hence, Ce based compounds are unconventional and interesting to study.

Here we report on exploratory studies on a new Ce compound namely $CeRhGa_4$. This compound crystallizes in an orthorhombic structure having structure type $CeOsGa_4$ belonging to the space group *Pmma* number 51. This structure of the 1:1:4 systems was first reported in 2002 [6].

2. Experimental Details

A polycrystalline sample of $CeRhGa_4$ was prepared from high-purity elements of Ce (99.999 %), Rh (99.97 %) and Ga (99.999 %). The rhodium powder was cold pressed to pellets. The 3

elements with a total weight of 2.0 g were mixed in the ratio of Ce:Rh:Ga = 1:1:4. These elements were placed on a water-cooled copper plate in arc-melting furnace (MAM-1 system manufactured by Edmund B*ü*hler GmbH) under ultra-high purity argon atmosphere. The elements were heated to reach melting point and turned over and re-melted several times to ensure homogeneity. The mass loss was calculated and found to be less than 2 %. The sample was characterized by powder X-ray diffraction (XRD), which was followed by Rietveld refinement profile using the Fullprof program [7]. This was necessary to investigate whether the sample was formed in the desired crystal structure as well as to check for possible impurities and parasitic phases. The sample was confirmed to be homogeneous using Energy Dispersive X-Ray Spectroscopy, with only minor inclusions which deviate from the desired stoichiometry. Since ascast-sample was found to be of a good quality, no annealing process was carried out. The $C_{\mathrm{p}}(T)$ was measured in a Physical Property Measurement System (PPMS) from Quantum Design (San Diego), which presents high stability controlled temperature (1.9 K - 390 K) and magnetic field (0 T - 9 T) environments. $M(\mu_0 H)$ and $\chi(T)$ measurements were conducted on the vibrating - sample magnetometer (VSM) platform of the same equipment over the temperature range of 1.9 K - 300 K.

3. Structural Properties

Figure 1 shows the XRD pattern along with the refinement fitting on XRD data of $CeRhGa_4$.

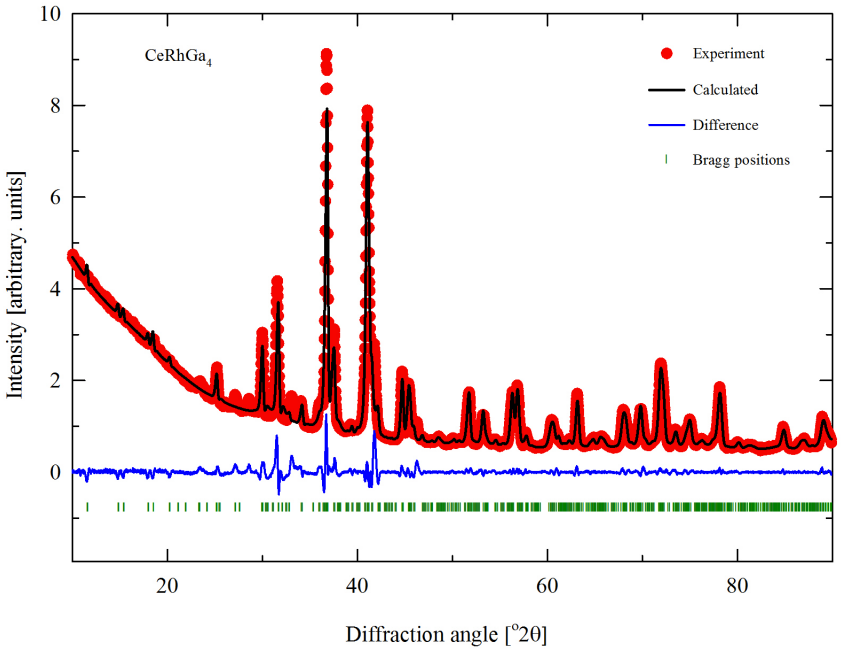

Figure 1. Powder X-ray diffraction pattern of $CeRhGa_4$ (red symbols) showing the Rietveld refinement profile shown by a black line, the difference between the calculated and the experimental intensities is indicated by a blue line and green vertical lines are the theoretical Bragg peak positions.

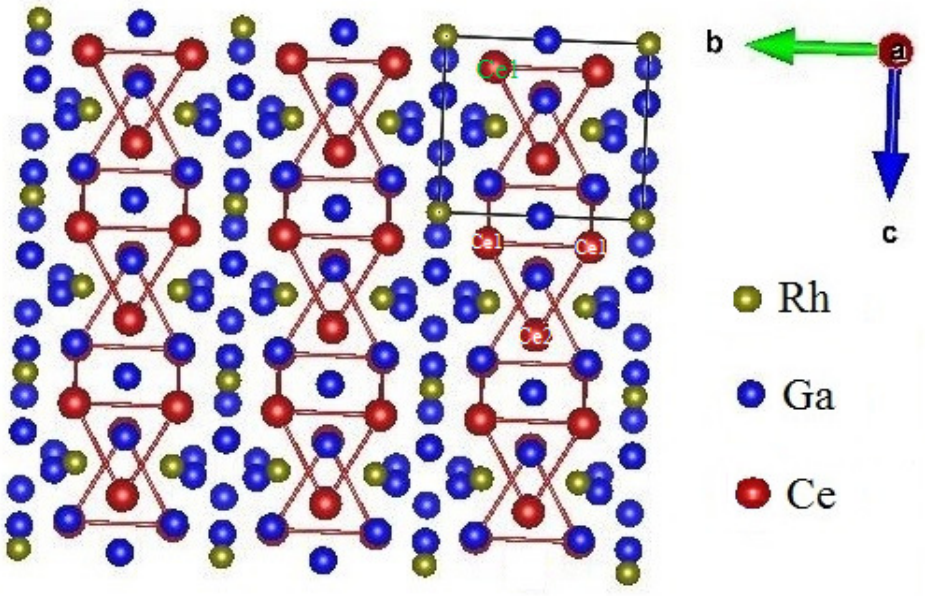

Figure 2. Crystal structure of $CeRhGa_4$ showing the location of atoms: cerium atoms are indicated by red spheres, blue spheres indicate gallium atoms and yellow spheres are rhodium atoms.

The refinement confirms that the compound is an orthorhombic structure with the $CeOsGa_4$ structure type [6]. The least-square refinement fit on XRD data yield the values of lattice parameters and are listed in Table 1. Figure 2 shows the crystal structure of the compound, having two Ce sites with their interatomic distances listed in Table 2, whilst the atomic coordinates are listed in Table 3.

Table 1. Crystal structure lattice parameters of $CeRhGa_4$ obtained from Rietveld refinement of the Powder X-ray diffraction pattern.

a (Å)	b (Å)	c (Å)	V (Å)^3
9. 5593(2)	8. 7441(2)	7. 6126(2)	636.3180(3)

Table 2. Interatomic distances in the structure of $CeRhGa_4$.

Atom	Interatomic distances (Å)
Ce1-Ce1	4.5053(0)
Ce1-Ce2	4.5512(0)
Ce1-Ga	3.1474(0)
Ce1-Rh	3.4740(0)
Ce2-Ga	2.9860(0)
Ce2-Rh	3.4773(0)

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Table 3. The atomic coordinates and Wyckoff site locations of $CeRhGa_4$ obtained from Rietveld refinement of the Powder X-ray diffraction pattern.

Atom	sites	x	y	z
Ce1	4 k	1/4	0.2598(3)	0.8251(3)
Ce2	2 f	1/4	1/2	0.3229(4)
Ga3	8 l	0.0753(1)	0.2520(5)	0.1714(5)
Ga4	4 k	1/4	0.1585(1)	0.5417(5)
Ga5	4 j	0.0597(5)	1/2	0.6277(5)
Ga6	4 i	0.0580(5)	0	0.3257(3)
Ga7	2 e	1/4	0	0.1382(4)
Ga8	2 b	0	1/2	0
Rh9	4 h	0	0.2556(2)	1/2
Rh10	2 a	0	0	0

4. Magnetic properties

The magnetic susceptibility, $\chi(T)$, of $CeRhGa_4$ measured in the temperature range of 2 to 300 K and in the field of 1 T is shown in Figure 2 (main panel).

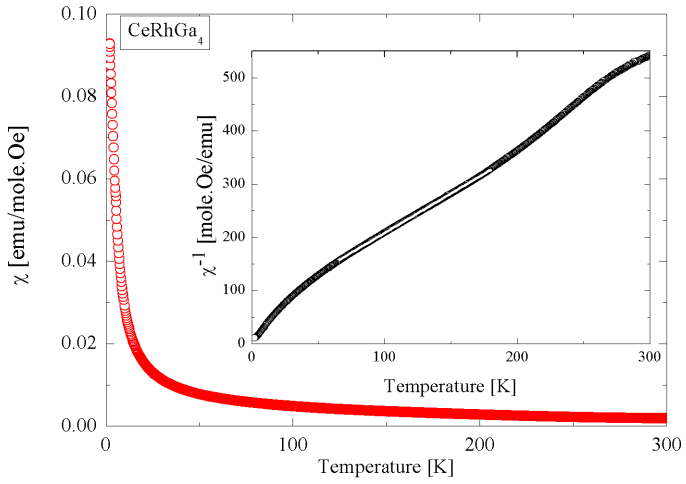

Figure 3. (Main panel) Temperature dependence of magnetic susceptibility, $\chi(T)$, of $CeRhGa_4$ measured in a field of 1 T. The inset shows the inverse magnetic susceptibility, with a white solid line representing a Curie-Weiss fit.

The data between 2 and 80 K, show no evidence of magnetic ordering, although a curvature deviating from Curie-Weiss behaviour is observed in this region. The inset shows the graph of $\chi^{-1}(T)$ in the temperature range, 2 to 300 K. The white solid line shows the Curie-Weiss fit for data in the temperature range ($80 > T < 180$ K), according to the expression $\chi^{-1}(T) = 3k_B(T - \theta_p)/\ N_A\mu^2{}_{eff}$. Data above 180 K deviates from the Curie-Weiss law and it is probably Crystal

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Electric Field. The parameters; k_B is the Boltzman constant, θ_p is the Weiss temperature, N_A is the Avogadro number and $\mu^2{}_{eff}$ is the effective magnetic moment. The data obey Curie-Weiss behaviour and resulted in the fitted Weiss temperature $\theta_p = -40.562(4)$ K and the effective magnetic moment $\mu_{eff} = 2.32(3)\ \mu_B$. The negative value of θ_p indicates that antiferromagnetic interactions are dominant at high temperatures. The fitted value of μ_{eff} is close to the theoretical value of the free Ce^{3+} ion, which is 2.54 μ_B/Ce.

Figure 4 (a) shows the magnetic field dependence of magnetization, increased curvature towards low temperature isotherms is observed. Furthermore, at 2 K it is observed that there is a tendency to saturate in high magnetic fields, whilst for isotherms between 10 and 20 K a simple paramagnetism is observed. Figure 4 (b) shows the saturation magnetization that decreases with an increase in temperature. These values were simply extrapolated from the slope (shown by black solid line in Figure 4 (a)) of the highest magnetic field measured to the obtained magnetization value. The saturation magnetization in this compound at 2 K is 0.35 μ_B/Ce, which is much less than the theoretical expected value of $g_J J = 2.14\ \mu_B$ for a free Ce^{3+} ion, which involves the entire six-fold J= 5/2 multiplet [8].

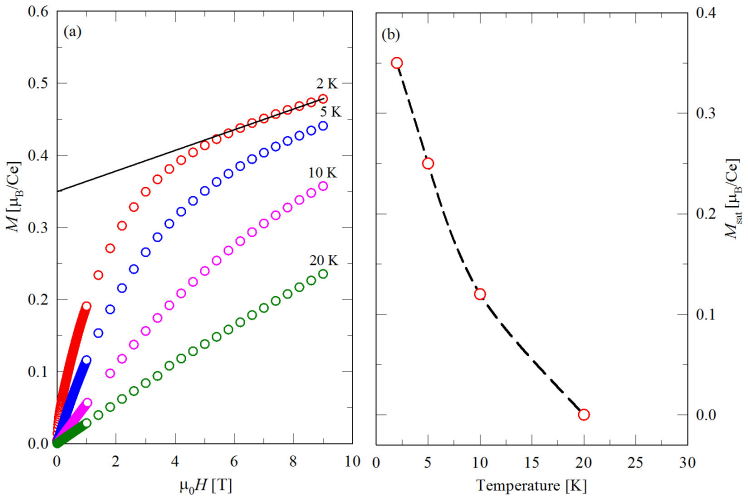

Figure 4. (a) Isothermal magnetization as a function of magnetic field upto 9 T within a temperature range of $T = 2$ and 30 K. (b) Variation of saturation magnetization as a function of temperature (2 to 30 K) evaluated from isotherm magnetization.

5. Specific heat

Figure 5 (a) presents the temperature dependence of specific heat, $C_p(T)$, measured in zero field showing a monotonous decrease of specific heat down to 2 K with no evidence of magnetic ordering. The dashed horizontal line represents the Dulong-Petit value $3NR$, where N is the number of atoms per formula unit and R is the universal gas constant. This data reached the Dulong-Petit value at 149.58 J/mol.K and it corresponds with the maximum specific heat obtained at room temperature, which is 150 J/mol.K. Figure 5 (b) shows the $C_p(T)/T$ vs T^2 data, with a Sommerfeld fit represented by a red solid line according to the expression $C_p(T)/T = \gamma + \beta T^2$, where γ is the Sommerfeld coefficient and β is the constant related to Debye temperature, θ_D, by $\beta = 12\pi^4 NR/5\theta_D$. The Sommerfeld coefficient was found to be γ = 0.1094(1) J/mol.K^2, whilst the calculated Debye temperature, $\theta_D = 268(1)$ K. The θ_D value

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indicates the total phonon contribution to the specific heat. The Sommerfeld coefficient value obtained confirms that this compound is not a usual metal as it is 150 times greater than the coefficient of the normal metal, for example, $\gamma_{Cu} = 0.69$ mJ/mol.K^2 [8]. Figure 5 (c) plots $C_p(T)/T$ vs T at different magnetic fields, throughout the measured temperature range the data confirms the absence of the magnetic ordering. Below $T = 5$ K, an upturn is observed in each measured field, further investigations using Helium-3 measurements are planned.

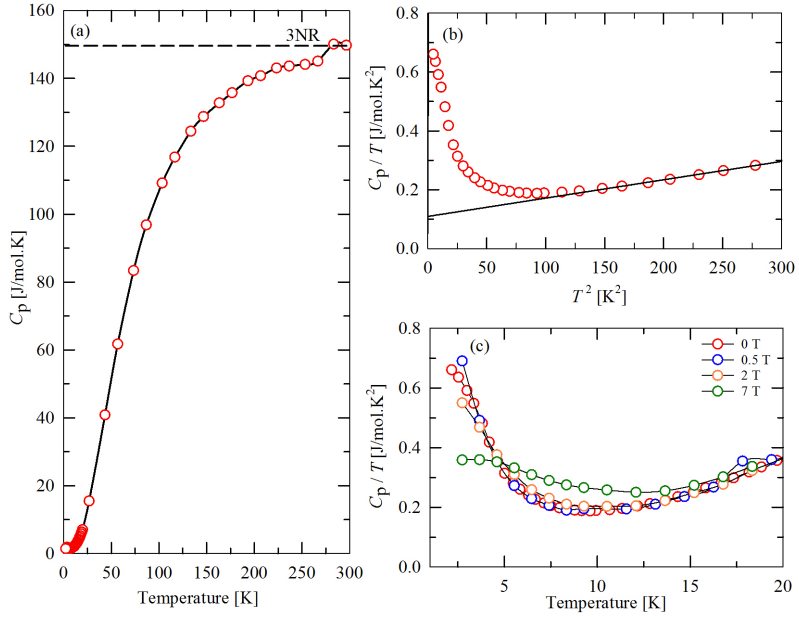

Figure 5. (a) Temperature dependence of specific heat measured under zero field. (b) $C_p(T)$ vs T^2 at zero-magnetic field with a black solid line showing a linear fit. (c) shows $C_p(T)/T$ vs T data measured at different fields.

6. Conclusions

$CeRhGa_4$ was confirmed to crystallize in an orthorhombic $CeOsGa_4$ type structure belonging to the space group *Pmma*, number 51. There is no detectable magnetic ordering observed from both $C_p(T)$ and $\chi(T)$ from room temperature to 2 K. Further measurements will be done towards lower temperatures to investigate the possible existence of magnetic ordering.

Acknowledgments

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