# Investigation of the magnetic ground state of $PrRu_2Ga_8$ compound

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Abstract. We have investigated the ground state properties of the orthorhombic structure compound PrRu<sub>2</sub>Ga<sub>8</sub> through electronic and magnetic properties studies. The compound crystallizes in the CaCo<sub>2</sub>Al<sub>8</sub>-type structure, belonging to space group *Pbam* (No. 55). The temperature dependence specific heat shows a  $\lambda$ -type anomaly at  $T_N = 3.3$  K, indicating a bulk phase transition probably of antiferromagnetic origin. At the Néel temperature  $T_N$ , the entropy approaches the value of 4.66 J/mol.K which is about 0.8 Rln(2), where R is the universal gas constant. The analysis of the low temperature specific heat gives  $\gamma = 46 \text{ mJ/mol.K}^2$ . The temperature dependence DC magnetic susceptibility  $\chi(T)$  confirms the anomaly at 3.3 K and follows the Curie-Weiss law for temperatures above 50 K, with the calculated effective magnetic moment,  $\mu_{\text{eff}} = 3.47(2) \ \mu_B/\text{Pr}$  and Weiss temperature  $\theta_p = -7.80(1)$  K. This effective magnetic moment value is in good agreement with the Hund's rule theoretical free-ion value of 3.58  $\mu_B$ for  $Pr^{3+}$ . The electrical resistivity data also shows an anomaly at  $T_N$  and a broad curvature at intermediate temperatures probably due to crystalline electric field (CEF) effects. The  $Pr^{3+}$ in this structure type has a site symmetry of  $C_s$  which predicts a CEF splitting of the J = 4multiplet into 9 singlets and thus rule out in principle the occurrence of spontaneous magnetic order. In this article we discuss the magnetic order in  $PrRu_2Ga_8$  in line with an induced type of magnetism resulting from the admixture of the lowest CEF level with the first excited state.

#### 1. Introduction

The  $\Pr T_2 X_8$  [T = Fe, Co, Ru, Rh; X=Al, Ga, In] family of compounds are quasi-skutterudites which crystallize in the orthorhombic CaCo<sub>2</sub>Al<sub>8</sub>-type structure with *Pbam* space group (No. 55) [1]. The structure of this family of compounds consists of caged network of atoms and belongs to a class of largely unexplored rare-earth intermetallic compounds. The Pr and Tatoms in this structure form a chain parallel to the *c*-axis and are both separated by the Ga atoms. The  $\Pr^{3+}$  ion has a site symmetry of monoclinic  $C_s$  in the crystal structure and as a consequence, the CEF splitting of the J=4 multiplet results in 9 singlets [2, 3]. In such systems, the ground state is expected to be a  $\Gamma_1$  singlet as dictated by  $\Pr^{3+}$  site symmetry. Hence, the occurrence of spontaneous magnetic order in this family especially where the rareearth site symmetry predicts a singlet ground state is unexpected. However, recent experimental studies have revealed that in exceptional cases, systems predicted to have a  $\Gamma_1$  singlet ground state eventually show a magnetic ordering at low temperatures [3–10]. Magnetism in these systems are largely attributed to induced moment magnetism due to the overcritical exchange interactions between the ground state singlet and the first excited state. In this article, we

 Table 1. Crystallographic parameters of PrRu<sub>2</sub>Ga<sub>8</sub> and LaRu<sub>2</sub>Ga<sub>8</sub> obtained from the Rietveld refinements.

Compound	PrRu <sub>2</sub> Ga <sub>8</sub>	$LaRu_2Ga_8$
Space group	<i>Pbam</i> (No. 55)	Pbam (No. 55)
a (Å)	12.607(3)	12.65(3)5
b (Å)	14.713(3)	14.715(5)
c (Å)	4.1010(2)	4.112(2)
V (Å <sup>3</sup> )	760.68(4)	766.90(1)
$R_p(\%)$	6.443	5.610
$R_{wp}(\%)$	8.392	8.237

present results of our investigation on the nature of the ground state in  $PrRu_2Ga_8$  compound, the crystal structure of which was first announced by Schlüter and Jeitschko [1].

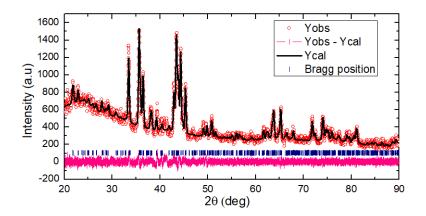
## 2. Experimental methods and crystal structure

Polycrystalline samples of PrRu<sub>2</sub>Ga<sub>8</sub> and LaRu<sub>2</sub>Ga<sub>8</sub> were prepared by arc melting stoichiometric amounts of Pr, La, Ru and Ga (4N) in an Edmund Bühler arc furnace by a method described in ref. [3]. Room temperature powder X-ray diffraction (XRD) was recorded using a Rigaku Smartlab diffractometer with  $Cu-K_{\alpha}$  radiation. The observed pattern for both samples correctly match that of the *Pbam* space group and no impurity phases were observed within the resolution limit of the instrument. A Rietveld refinement [11] using Fullprof prgram [12] was carried out on the patterns collected and the lattice parameters obtained are presented in Table 1 which are consistent with earlier reports [1, 3, 13]. The Rietveld refinement of the XRD pattern of PrRu<sub>2</sub>Ga<sub>8</sub> is shown in Fig. 1. In this structure, the shortest Pr-Pr separation is 4.080 Å (about 26% greater than the sum of two Pr ionic radii), Pr-Ga is 3.123 Å (about 7% greater than the sum of their ionic radii) and Pr-Ru is 3.101 Å (about 7% greater than the sum of their ionic radii). In view of this, the structure of PrRu<sub>2</sub>Ga<sub>8</sub> therefore resembles those of other caged compounds where the Pr atom is enclosed in an oversized cage network formed by Ru-Ga atoms. As stated above, the shortest Pr-Pr separation in the structure which is  $\sim 26\%$  is greater than the separation between the sum of two Pr ionic radii suggests that the Pr atoms are weakly bonding or may be out of reach of direct magnetic exchange due to no direct orbital overlap. A possible consequence of this will be the suppression of the magnetic transition temperature in systems with a magnetic order parameter in the ground state.

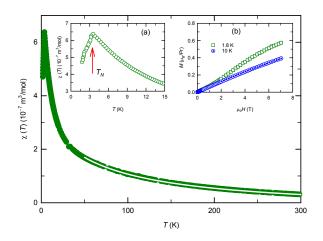
Magnetic properties have been measured using the Magnetic Property Measurement System (Quantum Design Inc. San Diego) between 1.9 K and 300 K with an external magnetic field up to 7 T. The electrical resistivity measurement from 300 K down to 1.9 K was taken using the conventional four probe DC method with contacts made using a spot welding equipment. Specific heat was measured using the quasi-adiabatic thermal relaxation method down to 0.4 K. Both the electrical resistivity and specific heat were measured using the Physical Property Measurement System also from Quantum Design.

## 3. Magnetic properties

The temperature dependence of magnetic susceptibility  $\chi(T)$  of PrRu<sub>2</sub>Ga<sub>8</sub> measured between 1.9 and 300 K is presented in Fig. 2. For temperatures above 50 K,  $\chi(T)$  could be fitted to the Curie-Weiss expression given by;  $\chi = N_A \mu_{\text{eff}}^2 / (3k_B(T - \theta_p))$ , where  $\mu_{\text{eff}}$  and  $\theta_p$  are the effective magnetic moment and Weiss temperature respectively, N<sub>A</sub> is the Avogadro's number and k<sub>B</sub> is the Boltzmann's constant. Values of  $\mu_{\text{eff}} = 3.47(2) \ \mu_B$  and  $\theta_p = -7.80(1)$  K are



**Figure 1.** Experimentally observed X-ray diffraction pattern of  $PrRu_2Ga_8$  (red circle) along with a Rietveld refinement profile (black line) based on the *Pbam* space group. The Bragg peaks are shown as blue vertical bars.

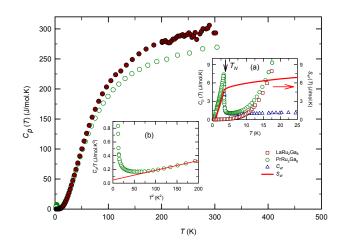


**Figure 2.** Temperature dependence of magnetic susceptibility  $\chi(T)$  of PrRu<sub>2</sub>Ga<sub>8</sub> together with a Curie-Weiss fit (white-solid line). Inset (a): Low-*T* of  $\chi(T)$  showing an antiferromagnetic ordering at  $T_N = 3.3$  K. (b): Isothermal magnetization of PrRu<sub>2</sub>Ga<sub>8</sub> at 1.8 K and 10 K.

obtained from the least-squares fit. The value of  $\mu_{\text{eff}}$  obtained is fairly reconcilable to the value of  $g_J\sqrt{J(J+1)}\mu_B = 3.58 \ \mu_B$  expected for a free  $\text{Pr}^{3+}$  ion. At ~ 3.3 K,  $\chi(T)$  develops an anomaly signalling a phase transition possibly of antiferromagnetic origin. The low temperature region of  $\chi(T)$  is expanded in inset (a) with the magnetic transition at  $T_N$  indicated by the arrow. In inset (b), the isothermal magnetization M(B) of  $\text{PrRu}_2\text{Ga}_8$  is presented in fields up to 7 T. At 1.8 K, an upward curvature in M(B) is seen near 2 T, while closer to 7 T the curvature turns slightly downward again mimicking saturation. The origin of these features are not immediately clear but appears to be matamagnetic in nature. The behaviour of M(B) in 10 K however follows a quasi-linear dependence with fields.

#### 4. Specific heat

The temperature dependence of specific heat  $C_p(T)$  of  $PrRu_2Ga_8$  and that of the nonmagnetic reference compound LaRu\_2Ga\_8 is presented in Fig. 3. In inset (a), the low temperature  $C_p(T)$  of  $PrRu_2Ga_8$  and LaRu\_2Ga\_8 together with the electronic contribution to specific heat



**Figure 3.** Temperature dependence of specific heat  $C_p(T)$  of  $PrRu_2Ga_8$  and  $LaRu_2Ga_8$ . Inset (a): Low- $T C_p(T)$  of  $PrRu_2Ga_8$  and  $LaRu_2Ga_8$ , electronic contribution to specific heat  $C_{4f}(T)$ and the magnetic entropy  $S_{4f}(T)$ . (b): Plot of  $C_p/T$  against  $T^2$  together with a Debye fit (red-solid line).

 $C_{4f}(T)$  obtained by subtracting the specific heat of LaRu<sub>2</sub>Ga<sub>8</sub> from that of the main compound  $PrRu_2Ga_8$  and the calculated entropy  $S_{4f}(T)$  are shown. A  $\lambda$ -type anomaly at  $T_N \approx 3.3$  K is clearly indicated by the arrow in the figure for both  $PrRu_2Ga_8$  and  $C_{4f}(T)$  data indicating a bulk phase transition.  $S_{4f}(T)$  is calculated using the expression;  $S_{4f}(T') = \int_0^{T'} C_{4f}(T)/T dT$ . The value of the entropy around  $T_N$  is 4.66 J/mol.K which is  $\simeq 80\%$  of Rln(2) expected for a doublet ground state. We note however that the full doublet entropy is only released at about 8 K. The estimation of  $C_{4f}(T)$  was only carried out up to about 24 K, above which the phonon specific heat dominates. Within this temperature range, a plot of  $C_{4f}(T)/T$  against  $T^2$ based on the expression  $C_{4f}(T)/T(T \rightarrow 0) \equiv \gamma$ , was found not to be an increasing function of T which consequently renders the extraction of the electronic Sommerfeld coefficient,  $\gamma$  from  $C_{4f}(T)$  difficult in the present case. We have therefore used the total specific heat in the estimation of  $\gamma$  as presented in inset (b) of Fig. 3 based on the expression  $C_p/T = \gamma + \beta T^2$ and  $\beta = 12\pi^4 n R/(5\theta_D^3)$ , where n and R are the number of atoms and Universal gas constant respectively. From the least-squares fit, a value of  $\gamma = 46.04(3) \text{ mJ/mol.K}^2$  and Debye temperature  $\theta_D = 248.1(2)$  K are obtained. The  $\gamma$  value obtained here is slightly enhanced compared to that found for ordinary metals which could be due to moderate heavy-electronlike behaviour in the system. The Sommerfeld coefficient  $\gamma$  has a direct relationship with the mass of the quasiparticles in a metal at low temperatures and it gives an idea about their degree of mass enhancement. We note that in a similar iso-structural compound  $PrCo_2Ga_8$ [14], an enhanced quasi-particle mass behaviour has been observed while on the other hand, iso-structural aluminides compounds like  $PrFe_2Al_8$  and  $PrCo_2Al_8$  [3, 13] have been reported to have  $\gamma$  values in the range of ordinary metals ( $\approx 10 \text{ mJ/mol.K}^2$ ).

### 5. Electrical Resistivity

The temperature dependence of electrical resistivity  $\rho(T)$  of PrRu<sub>2</sub>Ga<sub>8</sub> and LaRu<sub>2</sub>Ga<sub>8</sub> measured between 1.9 and 300 K is presented in Fig. 4. LaRu<sub>2</sub>Ga<sub>8</sub> shows a typical metallic behaviour from room temperature down to low temperatures with residual resistivity ratio (RRR) of 15.47.  $\rho(T)$ of PrRu<sub>2</sub>Ga<sub>8</sub> shows a broad curvature at intermediate temperatures and an anomaly indicating a phase transition at  $T_N \approx 3.3$  K. The RRR of  $\approx 6$  is observed which is lower compared to that of LaRu<sub>2</sub>Ga<sub>8</sub>. However, the RRR of both compounds suggest a reasonable good crystalline

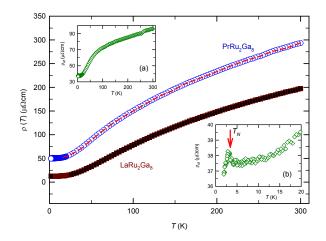


Figure 4. Temperature dependence of electrical resistivity  $\rho(T)$  of PrRu<sub>2</sub>Ga<sub>8</sub> and LaRu<sub>2</sub>Ga<sub>8</sub>. The red-dashed line is a BGM fit described in the text. Inset (a): Electronic contribution to resistivity  $\rho_{4f}(T)$ . (b): Low-T of  $\rho_{4f}(T)$  with an arrow indicating  $T_N = 3.3$  K.

quality. Furthermore, for temperatures above 10 K,  $\rho(T)$  of PrRu<sub>2</sub>Ga<sub>8</sub> was fitted to the Bloch-Grüneissen-Mott (BGM) model [15] as indicated by the red-dashed line. The BGM expression is given by;

$$\rho(T) = \rho_0 + \frac{4K}{\Theta_D} \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} + \alpha T^3, \tag{1}$$

where  $\rho_0$  is the residual resistivity due to defect scattering in the crystal lattice, K is the electronphonon coupling constant,  $\Theta_D$  is the Debye temperature and also contains a contribution from the electron-electron correlations [16, 17] while  $\alpha T^3$  is the Mott term which describes the *s*-*d* interband scattering. Values of  $\rho_0 = 49.522 \ \mu\Omega$  cm,  $K = 67.588 \ \mu\Omega$  cm K,  $\Theta_D = 41.162$  K and  $\alpha = -2.607 \times 10^{-6} \ \mu\Omega$  cm K<sup>-3</sup> are obtained from the fit. The electronic contribution to resistivity  $\rho_{4f}$  obtained by subtracting the phonon contribution from PrRu<sub>2</sub>Ga<sub>8</sub> is presented in inset (a) while (b) is the low temperature plot of  $\rho_{4f}$ .  $\rho_{4f}$  shows a strong temperature dependence from room temperature down to  $\approx 30$  K with a shallow curvature around 100 K. This feature likely originates from possible CEF effect on the resistivity. Below about 30 K, the resistivity is weakly temperature dependent down to  $\approx 5$  K, below which it rises into a peak centred at 3.3 K which is associated with the magnetic ordering at  $T_N$ .

#### 6. Discussion and conclusion

From the electronic and magnetic properties of  $PrRu_2Ga_8$ , a phase transition at  $T_N = 3.3$  K is observed. The magnetic ordering in  $PrRu_2Ga_8$  is at variance to the singlet ground state expected based on the  $C_s$  site symmetry of the  $Pr^{3+}$  in the  $CaCo_2Al_8$  structure type. Among other factors, induced magnetism is thought to have been responsible for such observation arising due to the admixture of the first excited CEF level with the ground state singlet when the exchange interaction exceeds a critical value based on the expression for self-induced moment ordering [4, 5];

$$T_c = \Delta \left[ \ln \frac{J_{ex} \alpha^2 + n\Delta}{J_{ex} \alpha^2 + n\Delta} \right]^{-1}, \qquad (2)$$

where  $\Delta$  is the energy splitting between the ground state singlet and the first excited state,  $\alpha$  is the matrix element between the ground state singlet and the first excited state, n is

the degeneracy of the first excited state,  $J_{ex}$  is the exchange interaction and  $T_c$  is the meanfield critical temperature. From inelastic neutron scattering (INS) experiment, the exchange interaction can therefore be estimated based on the above expression. In the present analysis, the exchange interaction can be predicted according to the expression;  $\theta_p = -J_{ex}J(J+1)/3k_B$ , where  $\theta_p = -7.8$  K as obtained from magnetic susceptibility analysis, and J = 4. The value of  $J_{ex} = 0.094$  meV is obtained which is of the same order magnitude with the ordering temperature found in PrRu<sub>2</sub>Ga<sub>8</sub>. An induced magnetic ordering is thus believed to be favoured when the value of 0.094 meV is comparable or greater than that estimated from the INS experiment. A  $\gamma$  value of 46 mJ/mol.K<sup>2</sup> indicates a possible moderate heavy-electron like behaviour in the material. The magnetic susceptibility follows the Curie-Weiss law for temperatures above 50 K and gives  $\mu_{\text{eff}} = 3.47 \ \mu_B/\text{Pr}$  which is close to that expected for a free  $\text{Pr}^{3+}$  ion. Magnetic phenomena in this system may therefore be expected to be governed by a stable and well-defined Pr local magnetic moment. Further measurements in fields and inelastic neutron scattering are required to further explore microscopic aspects and crystal field effects discussed in this article.

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## References

- [1] Schlüter M and Jeitschko W 2001 Inorg. Chem. 40 6362
- [2] Henderson B and Bartram R H 2005 Crystal-field engineering of solid-state laser materials (Cambridge University Press)
- [3] Nair H S, Ghosh S K, Kumar R and Strydom A M 2016 J. Phys. Chem. Solids 91 69
- [4] Adroja D T and Anand V K 2012 Phys. Rev. B 86 104404
- [5] Anand V K, Adroja D T, Bhattacharyya A, Hillier A D, Taylor J W and Strydom A M 2014 J. Phys.: Condens. Matter 26 306001
- [6] Schobinger-Papamantellos P, André G, Rodriguez-Carvajal J, Moze O, Kockelmann W, Tung L D and Buschow K H J 2001 J. Magn. Magn. Mater. 231 162
- [7] Blanco J A, Schmitt D and Sal J C J 1992 J. Magn. Magn. Mater. 116 128
- [8] Andres K, Bucher E, S Darack J P and Maita 1972 Phys. Rev. B 6 2716
- [9] Nair H S, Ogunbunmi M O, Kumar C M N, Adroja D T, Manuel P, Fortes D, Taylor J and Strydom A M 2017 J. Phys.: Condens. Matter 29 345801
- [10] Vejpravová J, J Prokleška V and Sechovský V 2007 J. Magn. Magn. Mater. 316 374
- [11] Thompson P, Cox D E and Hastings J B 1987 J. Appl. Crystallogr. 20 79
- [12] Rodriguez-Carvajal J 1990 satellite meeting on powder diffraction of the XV congress of the IUCr vol 127 (Toulouse, France:[sn])
- [13] Tougait O, Kaczorowski D and Noël H 2005 J. Solid State Chem. 178 3639
- [14] Ogunbunmi M O, Sondezi B M, Nair H S and Strydom A M 2018 Physica B 336 128
- [15] Mott N F and Jones H 1958 The Theory of the Properties of Metals and Alloys (Dover publications, inc., Oxford England)
- [16] Falkowski M and Strydom A M 2017 J. Phys.: Condens. Matter 29 395601
- [17] Pikul A P, Kaczorowski D, Plackowski T, Czopnik A, Michor H, Bauer E, Hilscher G, Rogl P and Grin Y 2003 Phys. Rev. B 67 224417