Crystal structure and thermodynamic properties of the non-centrosymmetric PrRu$_4$Sn$_6$ caged compound

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Abstract. PrRu$_4$Sn$_6$ is a tetragonal, non-centrosymmetric structure compound. It is isostructural to the extensively studied Kondo insulator CeRu$_4$Sn$_6$ which crystallizes in the YRu$_4$Sn$_6$-type structure with space group $I4\bar{2}m$. In this structure, the Pr atom fills the void formed by the octahedral Ru$_4$Sn$_6$ units which results in a tetragonal body-centred arrangement. Here we present reports on the physical and magnetic properties of PrRu$_4$Sn$_6$. The temperature dependences of specific heat, $C_p(T)$, electrical resistivity, $\rho(T)$, and magnetic susceptibility, $\chi(T)$, reveal the absence of a long-range magnetic ordering down to 2 K. $\chi(T)$ follows a Curie-Weiss behaviour above 100 K with an effective magnetic moment, $\mu_{\text{eff}} = 3.34 \mu_B$/Pr and paramagnetic Weiss temperature, $\theta_p = -19.47$ K indicating a dominant antiferromagnetic interaction. The magnetization at 2 K is quasi-linear in nature and attains a value of 0.86 $\mu_B$/Pr at 7 T which is well reduced compared to the calculated value of 3.32 $\mu_B$/Pr expected for a free Pr$^{3+}$ ion. This is attributed to possible magneto-crystalline anisotropy in the system. $C_p(T)$ indicates the presence of a optical-phonon mode which is supported by a glass-like thermal conductivity above $\sim$45 K. This observation is associated with caged structured compounds where the low-frequency optical-phonon mode of the guest atom interacts with the host lattice, resulting in the scattering of heat-carrying quasiparticles.

1. Introduction
The RRu$_4$Sn$_6$ ($R = \text{Y, La-Nd, Sm, Gd-Ho}$) series are intermetallic compounds which crystallize in the tetragonal YRu$_4$Sn$_6$-type structure with a non-centrosymmetric space group $I4\bar{2}m$ (No. 121) [1]. The structure was first reported by Venturini et al [2]. The crystal structure is made up of an octahedral Ru$_4$Sn$_6$ unit enclosing the guest $R$ atom. Crystal structures of this nature have generated much interest lately especially in the search for new superconductors [3, 4]. Also, the non-centrosymmetric nature of the space group is characteristic of certain superconductors where the mixing of the spin-singlet and spin-triplet Cooper pairing channels have been found to give rise to a two-component order parameter [5–7]. CeRu$_4$Sn$_6$ is a Kondo insulator, and it is the most extensively studied member of the series [8–11]. Other studies by Koch and Strydom reveal a magnetic ordering for the isostructural compounds of RRu$_4$Sn$_6$, with $R =$ Sm, Gd and Dy compounds at low temperatures while those of Nd, Tb and Ho compounds are paramagnetic down to 2 K [12].

As part of our search for Pr-based systems exhibiting novel ground states, we have synthesized a polycrystalline sample of PrRu$_4$Sn$_6$ and investigated its physical and magnetic properties. It is noted that the existence of PrRu$_4$Sn$_6$ was first reported by Zumdick and Pöttgen [1] but no
physical or magnetic properties have been reported thereafter. The Pr atom in this structure has a tetragonal site symmetry of $D_{2d}$ similar to those of the $\text{Pr}_3T_4X_{13}$ compounds, resulting in the crystal electric field splitting of the $J = 4$ multiplet into seven levels consisting of five singlets and two non-Kramers doublets.

2. Experimental methods
A polycrystalline sample of $\text{PrRu}_4\text{Sn}_6$ was prepared by arc melting stoichiometric amounts of high-purity elements (wt.% $\geq$ 99.9) on a water-cooled Cu plate under a purified static argon atmosphere in an Edmund Buehler arc furnace. The weight loss after melting was $\sim$ 0.05%. The arc-melted pellet was wrapped in Ta foil, placed in an evacuated quartz tube and annealed at 900°C for 21 days. A powder X-ray diffraction (XRD) pattern was recorded on a pulverized sample using a Rigaku diffractometer employing Cu-Kα radiation. The obtained powder XRD pattern was refined using the Rietveld method [13] employing the FullProf suite of programs [14]. We found that the compound was phase-pure within the limits of the resolution of the instrument. In Table 1, the atomic positions and lattice parameters obtained from the refinement are presented and are comparable with a previous report [1]. The refined XRD pattern and the crystal structure are shown in Fig. 1.

Magnetic properties were measured using the Magnetic Property Measurement System (Quantum Design Inc., San Diego) between 2 K and 300 K with an external magnetic field up to 7 T. The four-probe DC electrical resistivity, specific heat and thermal transport measurements between 2 K and 300 K were measured using the Physical Property Measurement System also from Quantum Design.

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3. Magnetic properties
The temperature dependence of magnetic susceptibility, $\chi(T)$, of $\text{PrRu}_4\text{Sn}_6$ in an external field of 0.1 T and in the temperature range of 2 K to 300 K is presented in Fig. 2. $\chi(T)$ shows a paramagnetic behaviour down to low temperatures with no indication of a long-range magnetic ordering observed. The white-solid line is a Curie-Weiss fit based on the expression:

$$\chi(T) = N_A \mu_{\text{eff}}^2 / (3k_B(T - \theta_p))$$

for data above 100 K with values of effective magnetic moment, $\mu_{\text{eff}} = 3.34 \mu_B$/Pr and Weiss temperature, $\theta_p = -19.47$ K. The observed $\mu_{\text{eff}}$ is close to the calculated value of 3.58 $\mu_B$/Pr expected for a free Pr$^{3+}$ ion. At low temperatures, a Van-Vleck paramagnetic behaviour in $\chi(T)$ suggests a nonmagnetic ground state in $\text{PrRu}_4\text{Sn}_6$. The isothermal magnetization at 2 K is presented in the inset (b) of Fig. 2. The magnetization follows a quasi-linear behaviour up to 7 T and attains a value of 0.86 $\mu_B$/Pr at 7 T which is well reduced compared to the saturation moment of 3.32 $\mu_B$/Pr expected for a free Pr$^{3+}$ ion implying a possible magneto-crystalline anisotropy in the compound.
Figure 1. (a): Powder X-ray diffraction pattern of PrRu$_4$Sn$_6$ (red circles) with a Rietveld refinement (black line) based on the $I4_{2}m$ space group (No. 121). The vertical bars are the Bragg peak positions while the grey line represents the difference between the experimental and calculated intensities. (b): Crystal structure of PrRu$_4$Sn$_6$ showing Pr atom being enclosed by the Ru$_4$Sn$_6$ octahedral unit.

Figure 2. Temperature dependence of magnetic susceptibility, $\chi(T)$, of PrRu$_4$Sn$_6$ measured in a field of 0.1 T. The white-solid line is a Curie-Weiss fit described in the text. Inset (b): Isothermal magnetization of PrRu$_4$Sn$_6$ at 2 K.

4. Specific heat

The temperature dependence of specific heat, $C_p(T)$, of PrRu$_4$Sn$_6$ studied between 2 K and 300 K is presented in Fig. 3. Inset (a) of Fig. 3 shows a plot of $C_p/T^3$ against $T$. Such a plot is important in determining the possible presence of low-frequency Einstein modes in $C_p(T)$ through the occurrence of a local maximum in $C_p/T^3$. A local minimum is observed in the plot as indicated by the arrow at $T_{\text{max}} = 6$ K which confirms the presence of low-frequency Einstein modes in PrRu$_4$Sn$_6$. $T_{\text{max}}$ is the temperature below which the Einstein modes are frozen out. By using a model incorporating both the Debye and Einstein terms, the experimental specific heat is fitted as shown by the red line in Fig. 3. The Debye-Einstein model is given by:

$$C_p(T) = mD \left( \frac{\theta_D}{T} \right) + nE \left( \frac{\theta_E}{T} \right),$$  \hspace{1cm} (1)
Figure 3. Temperature dependence of specific heat, $C_p(T)$, of PrRu$_4$Sn$_6$. Inset (a): Low-temperature plot of $C_p/T^3$ against $T$. Inset (b): Plot of $C_p/T$ against $T^2$ along with a linear fit indicated by the red-solid line to extract the Sommerfeld coefficient.

\[ D \left( \frac{\theta_D}{T} \right) = 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx, \]  

(2)  

\[ E \left( \frac{\theta_E}{T} \right) = 3R \left( \frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{(\exp(\theta_E/T) - 1)^2}, \]  

(3)  

where $\theta_D$ and $\theta_E$ are the Debye and Einstein temperatures with values of 241.73(9) K and 32.431(3) K, respectively. It is observed that $T_{\text{max}} \simeq 0.2 \theta_E$ which is in agreement with the observation in Ce$_3$Rh$_4$Sn$_{13}$ [15]. In Inset (b), a plot of $C_p/T$ against $T^2$ is shown together with a least-square fit (red line) 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 per formula unit and universal gas constant, respectively, $\gamma$ is the Sommerfeld coefficient and $\theta_D$ is the Debye temperature. Values obtained from the fit are: $\gamma = 38.60$ mJ/(K$^2$ mol) and $\theta_D = 154.50$ K. The $\gamma$ observed for PrRu$_4$Sn$_6$ is about 10 times the values found in ordinary metals.

5. Transport properties

To further understand the physical properties of PrRu$_4$Sn$_6$, a thermal transport measurement was carried out between 2 K and 300 K. The temperature dependences of thermoelectric power, $S(T)$, and thermal conductivity, $\kappa(T)$, were measured simultaneously on a bar-shaped sample. As shown in Fig. 4 (a), $S(T)$ is positive throughout the temperature range investigated and attains a value of 18.81 $\mu$V/K at room temperature. The red and black-dashed lines suggest two areas of linear-in-$T$ behaviour on either side of $\sim 135$ K. At 2 K, $S(T)$ has a value of $\sim 1$ $\mu$V/K indicating a significant drop in the carrier concentration between room temperature and 2 K. The change in slope of $S(T)$ at about 145 K is consistent with the anomaly observed in $C_p(T)$ around the same temperature. The origin of such an observation is not immediately clear and further measurements are needed to resolve the physics at play. A plot of $S(T)/T$ is shown in the inset of Fig. 4 (a). For $T \leq 100$ K the slope of $S(T)/T$ is $\sim 0.7$ $\mu$V/K$^2$ which is slightly above those of ordinary metals. The general feature of $S(T)$ suggests a hole-type charge carriers near the Fermi level.

The total thermal conductivity, $\kappa_T(T)$, of PrRu$_4$Sn$_6$ is presented in Fig. 4 (b) on a log-log
Figure 4. (a) Temperature dependence of thermoelectric power, $S(T)$, of PrRu$_4$Sn$_6$. The red and black-dashed lines are guides to the eye, indicating a change in slope of $S(T)$ at $\sim$145 K. Inset: Plot of $S/T$ against $T$ on a semi-log axis. (b) Temperature dependences of total thermal conductivity, $\kappa_T(T)$, phonon thermal conductivity, $\kappa_{ph}(T)$ and electronic thermal conductivity, $\kappa_E(T)$. The green, brown and blue dashed-lines represent the power-law behaviours of $\kappa_T(T)$, $\kappa_{ph}(T)$ and $\kappa_E(T)$, respectively while the black-dashed line is a guide to the eye described in the text. Inset: Temperature dependence of electrical resistivity with a BG fit (red line) described in the text.

$\kappa_T(T)$ is nearly temperature independent from room temperature down to about 45 K (as shown by the black-dashed line) which is characteristic of a glassy behaviour in thermal conductivity. The observation of a glass-like thermal conductivity in a crystalline compound is often associated with caged systems. The low-frequency optical-phonon mode of the guest atom scatters heat-carrying quasiparticles thus leading to a reduction in lattice thermal conductivity.

Using the Wiedemann-Franz relation [16] given as:

$$\kappa = L_0 T/\rho,$$

where $L_0$ is the Lorentz number given by:

$$L_0 = \pi^2 k_b^2 / 3 e^2 = 2.45 \times 10^{-8} \text{ Wm/K}^2,$$

the electronic contribution to the thermal conductivity, $\kappa_E(T)$, is extracted and it is also presented in Fig. 4 (b). Also shown in the plot is $\kappa_{ph}(T)$ obtained by subtracting $\kappa_E(T)$ from $\kappa_T(T)$. Below about 10 K, $\kappa_T(T)$ and $\kappa_{ph}(T)$ show power-law behaviour of $T^{1.5}$ while $\kappa_E(T)$ is linear-in-$T$ as indicated by the green, brown and blue-dashed lines. This indicates a good metallic behaviour. $\kappa_{ph}(T) > \kappa_E(T)$ in the whole temperature range studied revealed that the heat transport is not charge-carrier dominated.

The temperature dependence of electrical resistivity, $\rho(T)$, of PrRu$_4$Sn$_6$ is presented in the inset of Fig. 4 (b) between 2 K and 300 K. $\rho(T)$ follows a typical metallic behaviour down to low temperature with residual resistivity ratio $\approx$ 5 which indicates a good crystalline quality. No signature of long-range magnetic or any type of ordering is observed in the temperature range studied in support of the observations in $\chi(T)$ and $C_p(T)$. To further understand the electrical transport properties of PrRu$_4$Sn$_6$, the Bloch-Grüneisen (BG) expression [17] was fitted to the data in the whole temperature range (shown as a red line). The BG expression is given as:

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

where $\rho_0$ is the residual resistivity due to defect scattering in the crystal lattice, $K$ is the electron-phonon coupling constant and $\Theta_R$ is the resistivity Debye temperature. Values of $\rho_0 = \ldots$
102.8(2) $\mu\Omega$ cm, $K = 90.19(1) \mu\Omega$ cm K, and $\Theta_R = 39.20(1)$ K are obtained from the least-square fit. This observation here further supports a metallic behaviour of PrRu$_4$Sn$_6$.

6. Conclusion
We have studied the physical and magnetic properties of the non-centrosymmetric PrRu$_4$Sn$_6$ compound. A paramagnetic ground state is inferred from the magnetic susceptibility results down to 2 K. The presence of low-frequency Einstein modes are observed in $C_p(T)$. This observation is further supported by the glass-like thermal conductivity for temperatures above 45 K. $S(T)$ undergoes a change in slope at $\sim 145$ K, which is around the same temperature an anomaly in $C_p(T)$ is observed. Further measurements are expected to help clarify the origin of the observations in $C_p(T)$ and $S(T)$.

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References