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Anisotropic physical properties of $PrRhAl_4Si_2$ single crystal: A non-magnetic singlet ground state compound

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ABSTRACT

We have grown the single crystal of $PrRhAl_4Si_2$, which crystallizes in the tetragonal crystal structure. From the low temperature physical property measurements like, magnetic susceptibility, magnetization, heat capacity and electrical resistivity, we found that this compound does not show any magnetic ordering down to 70 mK. Our crystal field calculations on the magnetic susceptibility and specific heat measurements reveal that the 9-fold degenerate $(2J+1)$ levels of Pr atom in $PrRhAl_4Si_2$ split into 7 levels, with a singlet ground state and a well-separated excited doublet state at 123 K, with a overall level splitting energy of 320 K.

1. Introduction

The rare earth ion Pr based intermetallic compounds typically order magnetically, the exchange coupling between the localized Pr magnetic moments is provided by the indirect RKKY exchange interaction. Since Pr ($4f^2$) is a non-Kramer's ion, some compounds of Pr with a singlet crystal electric field (CEF) ground level show Van Vleck paramagnetism and do not order magnetically. It is therefore of interest to explore the magnetic behaviour of new Pr compounds. The interest in Pr compounds is further heightened by the observation of heavy fermion superconductivity in $PrOs_4Sb_{12}$ in which the superconductivity has been attributed to a possible quadrupolar Kondo effect associated with a nonmagnetic Γ^3 doublet ground state [1–4]. More recently, heavy fermion superconductivity in $PrTi_2Al_{20}$ under pressure in the vicinity of the quantum critical point of the quadrupolar order and heavy fermion superconductivity in the quadrupole ordered state of PrV_2Al_{20} under ambient pressure have been observed [5–7]. Recently, we have been investigating the anisotropic magnetic properties of $RRhAl_4Si_2$ (R=Ce and Eu) and observed interesting magnetic behaviours in these compounds [8–10]. In continuation to our studies on this type of compounds and to understand the crystal electric field level schemes in the non-Kramer's Pr-based intermetallic compound, in this communication we report the magnetic properties of a new compound $PrRhAl_4Si_2$. The compound is isomorphic with the previously known $RRhAl_4Si_2$ (R=La, Ce and Eu) compounds [8]. Unlike the Ce and Eu compounds which order magnetically, due to the trivalent Ce-atom and the divalent Eu-atom, $PrRhAl_4Si_2$ is a Van Vleck paramagnet; heat capacity measurements down to 70 mK do not reveal any evidence for a magnetic or quadrupolar transition.

2. Experimental

Single crystals of $PrRhAl_4Si_2$ were grown by high temperature solution growth method using Al–Si eutectic as flux. The crystal was grown using the same protocol as already described for $EuTAl_4Si_2$ (T=Rh and Ir) [8]. In short, we have taken the stoichiometric ratio of high purity Pr, Rh, Al and Si elements in the ratio 1:1:4:2, together with the excess Al:Si eutectic (88:12) in a high quality recrystallized alumina crucible, which was subsequently sealed in a quartz ampoule under a vacuum of 10^{-6} Torr. The ampoule was heated to 1050 °C and held at this temperature for homogenization. Then the furnace was slowly cooled at the rate of 2 °C/h down to 730 °C at which point the quartz ampoule was quickly removed from the furnace and introduced in a centrifuge which was quickly spun to a rotating speed of 1000 rpm to remove the eutectic Al:Si flux which melts at 577 °C. A small

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amount of quartz wool, placed near the neck of the crucible, acts as a filter. Several flat platelet like single crystals with very shiny metallic luster, of dimensions of approximately $5 \times 5 \times 0.6$ mm^3 were obtained. Powder x-ray diffraction was used to check for phase purity, crystal symmetry and lattice parameters, while Laue diffraction was employed to establish the single crystal nature of the sample and to orient the crystal along the desired direction using a spark erosion cutting machine. Quantum design superconducting quantum interference device (QD SQUID) and vibrating sample magnetometer (VSM) were used to measure the magnetization, while the data on heat capacity and electrical resistivity were taken on quantum design physical properties measurement systems (QD PPMS). The heat capacity of $PrRhAl_4Si_2$ was measured down to 70 mK using the dilution insert of the QD-PPMS.

3. Results and discussion

3.1. Structure

Since the crystals of $PrRhAl_4Si_2$ were grown with off-stoichiometric ratio, the phase purity of the grown crystals was first confirmed by powder x-day diffraction. The x-ray diffraction pattern of $PrRhAl_4Si_2$ along with the results of Rietveld refinement is shown in Fig. 1. The x-ray diffraction pattern is similar to that of $RRhAl_4Si_2$ (R=La, Ce and Eu) with a slight deviation in the peak position due to the difference in the lattice parameters. From the Rietveld refinement it is confirmed that $PrRhAl_4Si_2$ crystallizes in the tetragonal crystal structure with the space group $P4/mmm$. The estimated lattice parameters are $a=4.210(2)$ Å and $c=8.068(3)$ Å. The lattice parameters are slightly lower than the corresponding values in $CeRhAl_4Si_2$, which is in accordance with the lanthanide contraction. Well-defined Laue diffraction patterns, together with the 4-fold symmetry confirmed the tetragonal crystal structure. The flat plane of the crystal has been identified as the (001) plane.

3.2. Magnetization

The inverse magnetic susceptibility, χ^{-1}, measured in the temperature range from 1.8 to 300 K is shown in Fig. 2, while the susceptibility, χ, is plotted in the inset. The susceptibility is anisotropic and a fit of Curie–Weiss expression to the inverse susceptibility from 150 to 300 K provides the following parameters: $\mu_{eff} = 3.45$ and 3.86 μ_B/Pr and $\theta_p = 13$ and -126.2 K for $H \parallel$ [100] and [001], respectively. The paramagnetic Weiss temperature θ_p along [001] is almost an order of magnitude larger than its value along [100] and is of opposite sign, indicating anisotropic magnetic

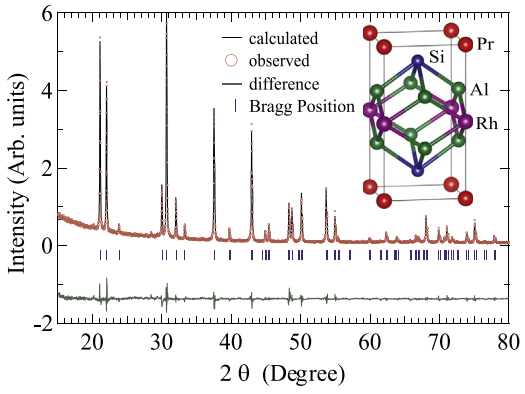

Fig. 1. (Color online) Powder x-ray diffraction pattern of $PrRhAl_4Si_2$ and the Rietveld analysis.

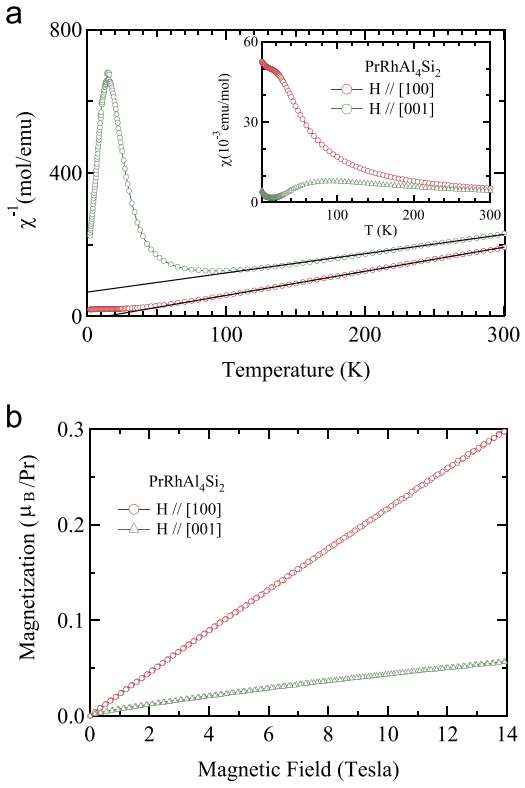

Fig. 2. (Color online) (a) Inverse magnetic susceptibility and susceptibility (in inset) up to 300 K of $PrRhAl_4Si_2$. (b) Isothermal magnetization measured at 2 K along the two principal crystallographic directions.

behaviour of this compound. Typically, the negative value of θ_p symbolizes the antiferromagnetic nature of the magnetic ordering. However, in $PrRhAl_4Si_2$, no magnetic ordering down to 70 mK, the large negative value of θ_p should then be ascribed to the crystal field effects and cannot be attributed to the molecular field. Furthermore, it characterizes the splitting between the ground state and the first excited state. At low temperatures when $\Delta/T \geq 1$, a plateau in the susceptibility is generally observed, here Δ refers to the energy splitting between the ground state and the first excited state. A plateau like feature is observed for $H \parallel$ [100], in Fig. 2(a) (inset), when there is a deviation in the Curie–Weiss law below 100 K. Similarly, in the orthogonal direction for $H \parallel$ [001], a subtle maximum is observed at temperature below which there is a deviation from the Curie–Weiss law. This results from the crystal field effects. Similar kind of feature is observed in the magnetic susceptibility of Pr_2CuO_4 [12]. The μ_{eff} is comparable to the Hund's rule derived value for Pr^{3+} magnetic moment. The prominent peak in χ^{-1} along [001] may be taken to be a signature of a magnetic transition but the plots of χ vs. T do not suggest any magnetic ordering (heat capacity data described below do not provide any evidence for a long range magnetic transition). The χ along both the directions tends to attain a limiting value at low temperatures; the upturn below 10 K may partly be due to the presence of some paramagnetic impurities. Also, the inverse magnetic susceptibility deviates from the linearity below 100 K, revealing that the degenerate $J=4$ multiplet is split by the crystal electric field separation with a separation energy of about 100 K. As mentioned in the beginning, a non-magnetic singlet ground state is possible in Pr compounds; a non-magnetic quadrupolar doublet can also give rise to a paramagnetic ground state. We show later from our crystal electric field (CEF) calculation that the anisotropy in the magnetic susceptibility is well explained and the ground state is a singlet state.