Journal of Physics: Conference Series **568** (2014) 042027 doi:10.1088/1742-6596/568/4/042027

Anomaly of Specific Heat in High Quality Single Crystal of $PrAg_2In$

Y Sato[1], H Morodomi[1], Y Inagaki[1], T Kawae[1], H S Suzuki[2]

[1]Department of Applied Quantum Physics, Kyushu university, Motooka, Fukuoka, 819-0395, Japan

[2]National Institutes for Material Science, Tsukuba, Ibaraki, 305-0047, Japan

E-mail: y.sato.483@s.kyushu-u.ac.jp

Abstract. $PrAg_2In$ has a non-Kramers doublet Γ_3 ground state, which is expected to show a quadrupolar phenomena. Although many studies have been devoted to investigate the novel features of $PrAg_2In$, there is no clear result how to remove the degeneracy of quadrupolar moment because this compound has a Heusler structure, in which the substitution between Pr and In ions is inevitable. We therefore prepare a high quality single crystal of $PrAg_2In$ with the residual resistivity ratio of 14, which is much larger than that of the previous samples. We measure the magnetic susceptibility with the SQUID magnetometer down to $T = 0.4$ K and the specific heat in the magnetic fields up to $H = 8$T along [100] crystal direction down to $T = 0.1$ K. The susceptibility is consistent with the CEF calculation. The specific heat shows a sharp peak at around $T_P = 0.33$ K. When the magnetic field is applied, the peak at T_P does not move up to $H = 2.5$ T. In contrast, it shifts to higher temperatures with broadening above $H = 2.5$ T. The broad peak above $H = 2.5$ T is well reproduced by the Schottky specific heat due to the splitting of the Γ_3 doublet in the magnetic fields. From these results, we conclude that a phase transition related to the Γ_3 doublet occurs at around T_P.

1. Introduction

In $4f$-electron systems, the spin-orbital interaction is larger than the crystalline-electric-field (CEF) effect so that the magnetic properties of $4f$-electrons are characterized by the total angular momentum $\boldsymbol{J}(= \boldsymbol{L} + \boldsymbol{S})$. For Pr-compound, a trivalent Pr ion forms $4f^2$ configuration in a crystal, indicating that the ninefold degenerate $J = 4$ multiplet is a ground state of the trivalent Pr ion. If the crystal structure of the trivalent Pr ion has a cubic symmetry, $J = 4$ multiplet splits into four levels: a singlet Γ_1, a doublet Γ_3, a triplet Γ_4 and a triplet Γ_5 by the cubic CEF effect.

A cubic compound of $PrAg_2In$ has the non-Kramers doublet Γ_3 ground state, which carries two quadrupolar moments; $O_2^0(= [3J_z^2 - \boldsymbol{J}]/2)$ and $O_2^2(= \sqrt{3}[J_x^2 - J_y^2]/2)$, and one octapolar moment $T_{xyz}(= \sqrt{15}/6\overline{J_xJ_yJ_z})$. The overline on the product denotes the operation of taking all possible permutations in terms of cartesian components, e.g., $\overline{J_xJ_y} = J_xJ_y + J_yJ_x$. The first report by Yatskar *et al.* showed no sign of quadrupolar ordering down to $T = 50$ mK [1]. Thus, it is very interesting how to dissolve the non-Kramers doublet degeneracy in $PrAg_2In$. In previous studies, a large Sommerfeld coefficient $\gamma \sim 6.5$ J/(mol K^2) and an anomalous logarithmic temperature dependence of the magnetic susceptibility are observed [1, 2]. Therefore,

the quadrupolar Kondo effect [3] is discussed as the origin of a heavy fermion behavior with the large γ value.

The sample quality is crucial to investigate the quadrupolar phenomena. For example, we report that the antiferro-quadrupolar(AFQ) transition temperature $T_Q = 0.4$ K in in $PrPb_3$ compound is suppressed to $T_Q = 0.28$ K only by 1% nonmagnetic La substitution of Pr [4]. Moreover, $PrAg_2In$ is a Heusler alloy, implying that the displacement between Pr-ion and In-ion occurs easily. Hence, it is difficult to distinguish the essential features from the effects such as the randomness, the presence of the grain boundaries, and the site-disorder. These show that the improvement of the sample quality is essential for studying the nature of the Γ_3 doublet ground state in $PrAg_2In$.

2. Experimental

We prepare a new single crystal by the Bridgeman method using a Mo crucible and a Ar arc melting. The residual resistivity ratio of the new sample is about 14, which is much larger than that of the previous ones with about 2–3. This strongly suggests the sample quality is improved enormously.

We study the DC magnetic susceptibility and the specific heat in the magnetic fields along [100] direction with the new sample of $PrAg_2In$. The DC magnetic susceptibility is measured by the Quantum Design SQUID magnetometer with a home-made ^{3}He insert [5]. The insert is made from a thin-walled stainless steel pipe with an inner diameter of 6.2 mm and is easily attached to the SQUID magnetometer in a few minutes. ^{3}He gas is condensed in the pipe, which is liquefied by ^{4}He gas at $T = 1.8$ K generated by the magnetometer via the heat exchanger of a Cu vacuum jacket with an outer diameter of 8.6 mm soldered to the stainless steel pipe. This system enables us to measure the DC magnetization down to $T = 0.4$ K with a high resolution $\sim 10^{-7}$ emu.

The specific heat is measured by a pseudo-adiabatic heat pulse method with a ^{3}He–^{4}He dilution refrigerator from $T = 0.1$ K to 1.2 K and a superconducting magnet up to $H = 8$ T along [100] crystal direction.

3. Results and Discussion

We show the temperature dependence of the DC magnetic susceptibility of $PrAg_2In$ at $H = 0.5$ T in Fig.1. The susceptibility above 15 K follows the Curie-Weiss law and is well reproduced by the CEF level scheme with Γ_3(0K)–Γ_4(75K)–Γ_5(145K)–Γ_1(181K). In contrast with the CEF calculation which the susceptibility gradually approaches a constant value below $T = 15$ K, the magnetic susceptibility shows a logarithmic temperature dependence down to $T = 0.4$ K. It is worthy to note that the same non-Fermi-liquid behavior of the DC magnetic susceptibility M/H is observed in other Pr-based compounds with the Γ_3 doublet in the CEF ground state [7, 8].

In Fig.2, we show the temperature dependence of the specific heat in zero field together with the previous result by Yatskar *et al.* [1]. The specific heat in zero field clearly shows a peak at around $T_p = 0.33$ K. Compared with the previous result, the peak becomes sharp and the maximum value grows to ~ 3 J/(mol K) from ~ 2 J/(mol K) at around 0.4 K. These features are identical to $Pr_{1-x}La_xPb_3$ system, in which the AFQ transition peak broadens with increasing the La-concentration [4]. These facts indicate that the quality of the new sample is largely improved and the observed features are the essential nature of $PrAg_2In$.

Next, we study the magnetic field dependence of $PrAg_2In$ to clarify the origin of the peak at around T_P. The magnetic filed is applied in [100] crystal direction up to $H = 8$ T. When the magnetic field is increased, the peak at T_P does not move up to $H \sim 2.5$ T as shown in Fig.3. Above $H \sim 2.5$ T, the peak shifts to higher temperatures with broadening. To understand the origin of the broad peak at high fields, we fit the experimental results using the nuclear specific

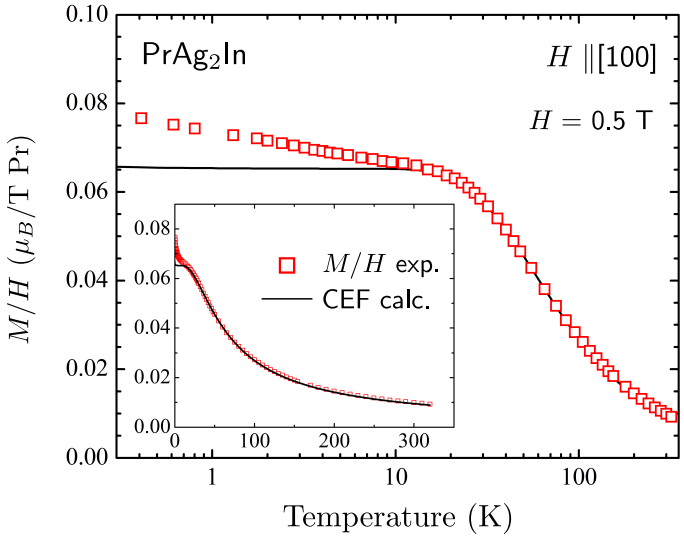

Figure 1. Temperature dependence of the magnetic susceptibility of $PrAg_2In$ at $H = 0.5$ T. Solid line shows the calculation result by CEF model with CEF parameter [6] of $x = 0.39$, $W = -2.30$ K.

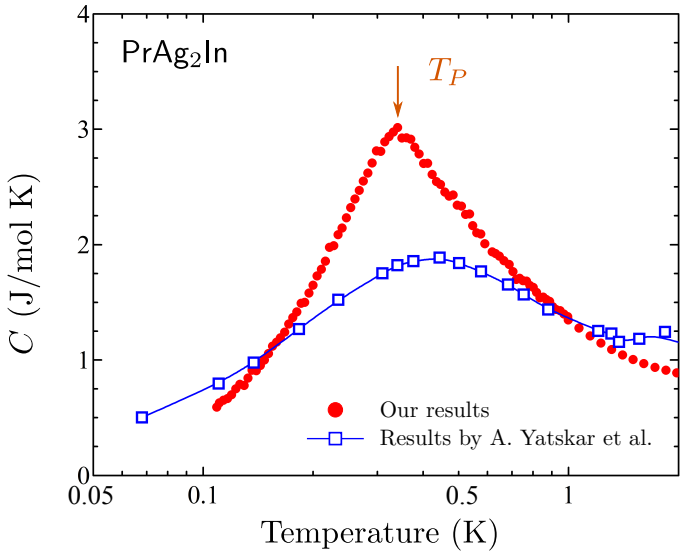

Figure 2. Temperature dependence of the specific heat of $PrAg_2In$. The red solid circle shows the results of this measurements and the blue open square shows the results by A. Yatskar *et al.* [1].

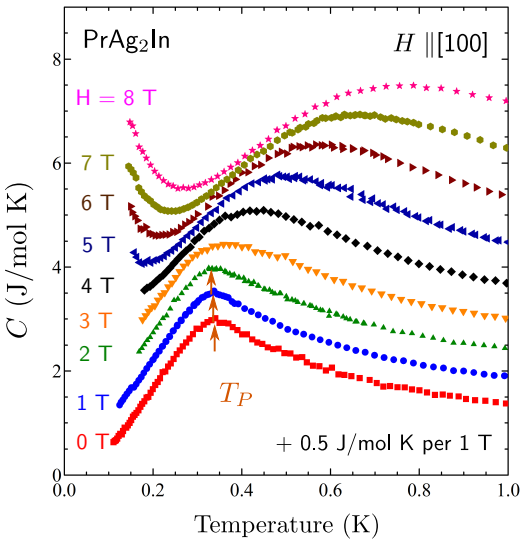

Figure 3. Temperature dependence of the specific heat of $PrAg_2In$ in the magnetic fields along [100] direction. The data from bottom to top show $H = 0$ T to 8 T per 1 T, which are shifted by 0.5 J/(mol K), respectively.

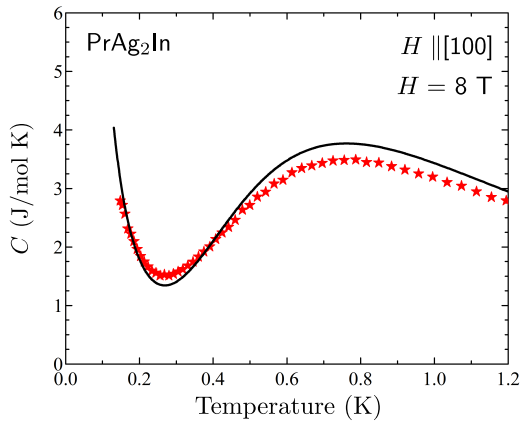

Figure 4. The Schottky peak fitting for the experimental results at $H = 8$ T(red star). The solid line is obtained using a eq.(1) with $\Delta = 1.87$ K and $A_n = 0.069$ J·K/mol .

heat and the two-level Schottky model expressed by the following equation:

$$\begin{aligned} C &= C_{\text{nuclear}} + C_{\text{schottky}}, \\ &= \frac{A_n}{T^2} + R\left(\frac{\Delta}{T}\right)\frac{\exp\left(\Delta/T\right)}{\left[1+\exp\left(\Delta/T\right)\right]^2}, \end{aligned} \tag{1}$$

where R is the gas constant with the value of 8.314 J/(mol K). We can reproduce well the experimental results at $H = 8$T with $\Delta = 1.87$ K and $A_n = 0.069$ J·K/mol. On the other hand, the splitting of the Γ_3 doublet at $H = 8$ T is calculated to be $\Delta_{\text{CEF}} = 1.58$ K by the CEF scheme obtained by the magnetic susceptibility measurements. This demonstrates that the broad peak is caused by the splitting of the Γ_3 doublet by the magnetic fields. From these results, we conclude that the sharp peak at around T_P is caused by a phase transitions, such as quadrupolar or octapolar orderings, related to the Γ_3 doublet.

4. Conclusion

We measured the temperature dependence of magnetic susceptibility at $H = 0.5$ T and the specific heat up to $H = 8$ T along [100] direction with a high quality single crystal of $PrAg_2In$. Above $T = 15$ K, the magnetic susceptibility is well reproduced by the CEF level scheme with a non-Kramers Γ_3 doublet ground state. In the specific heat, a sharp peak appears at around

$T_P = 0.33$ K. In the magnetic fields, the peak at T_P does not move up to $H = 2.5$ T. In contrast, it shifts to higher temperatures above $H = 2.5$ T with broadening. The broad peak at high magnetic fields is in good agreement with the Schottky specific heat due to the splitting of the Γ_3 doublet by the magnetic fields. From these results, we conclude that a phase transition related to the Γ_3 doublet occurs at around T_P.

References

[1] Yatskar A, Beyermann W P, Movshovich R, and Canfield P C 1996 *Phys. Rev. Lett.* **77** 3637.
[2] Tanida H, Takagi S, Suzuki H S, Satoh I and Komatsubara T 2006 *J. Phys. Soc. Jpn.* **75** 074721.
[3] Cox D L, 1987 *Phys. Rev. Lett.* **59** 1240.
[4] Kawae T, Shimogai M, Mito M, Takeda K, Ishii H, and Kitai K, 2001 *Phys. Rev.* B **65** 012409.
[5] Sato Y, Makiyama S, Sakamoto Y, Hasuo T, Inagaki Y, Fujiwara F, Suzuki H S, Matsubayashi K, Uwatoko Y, and Kawae T 2013 *Jpn. J. Appl. Phys.* **52** 106702.
[6] Lea K R, Leask M J M, and Wolf W P 1962 *J. Phys. Chem. Solids* **23** 1381.
[7] Tanida H, Suzuki H S, Takagi S, Onodera H, and Tanigaki K 2006 *J. Phys. Soc. Jpn.* **75** 073705.
[8] Kawae T, Koga M, Sato Y, Makiyama S, Inagaki Y, Tateiwa N, Fujiwara T, Suzuki H S, and Kitai T 2013 *J. Phys. Soc. Jpn.* **82** 073701.