Thermal properties of the nonmagnetic cubic $\Gamma_3$ Kondo lattice systems $\text{Pr}T_{r}2\text{Al}_{20}$ ($Tr = \text{Ti}, \text{V}$)

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Abstract. We report the results of the specific heat measurements for $\text{Pr}T_{r}2\text{Al}_{20}$ ($Tr = \text{Ti and V}$), both of which have the cubic nonmagnetic $\Gamma_3$ ground state of the crystal electric field scheme. Sharp peak anomalies observed at $T = 2.0$ K for $\text{PrTi}_2\text{Al}_{20}$ and $0.6$ K for $\text{PrV}_2\text{Al}_{20}$ indicate the second order phase transition due to the multipole degree of freedom. The application of the magnetic field along $[111]$ does not change the anomalies observed in the specific heat of either $\text{PrTi}_2\text{Al}_{20}$ or $\text{PrV}_2\text{Al}_{20}$, suggesting the quadrupole nature of the phase transition. A large Sommerfeld coefficient found above the ordering temperature in $\text{PrTi}_2\text{Al}_{20}$ suggests heavy quasi particle formation due to the scattering process of conduction electrons by quadrupole moments.

1. Introduction
A various interesting phenomena associated with the Kondo effect have been discovered in condensed matter physics such as heavy Fermions, Kondo insulators, quantum criticality and unconventional superconductivity. The Kondo effect in these systems is normally regarded as the “magnetic” Kondo effect since conduction ($c$) electrons screen the $f$ electrons’ magnetic dipole degree of freedom. Therefore, an important question is whether a “nonmagnetic” analog of the Kondo effect is possible by using multipole degree of freedom. Theoretically, Cox predicted that quadrupole moments, which may have two channels for hybridization, can be over-compensated by the $c$ electrons when the $f^2$ ion has a cubic symmetry and crystal electric field (CEF) ground state is cubic nonmagnetic $\Gamma_3$ [1]. According to this theory, the ground state is no longer a Fermi liquid and anomalous metallic behaviors appear as a result of the quadrupolar Kondo effects [2].

Experimentally, there have been a few studies on a Pr-based cubic compound with the nonmagnetic $\Gamma_3$ ground CEF state such as $\text{PrInAg}_2$, $\text{PrMg}_3$ and $\text{PrPb}_3$ [3, 4, 5]. These report a large enhancement of the Sommerfeld coefficient and discuss the possibility of a heavy fermion state due to the quadrupolar Kondo effects. However, the origin of the enhanced specific heat is still controversial partly because the degeneracy of the non-Kramers $\Gamma_3$ doublet can be easily lifted by structural disorder or distortion. On the other hand, if the system with the $\Gamma_3$ CEF ground doublet exhibits a quadrupole long-range order, it ensures that the degeneracy remains at least down to the transition temperature. Therefore, if we find a system that shows quadrupolar ordering and strong hybridization effect, it might allow us to observe Kondo effects based on the quadrupolar degree of freedom above the transition temperature.

$\text{Pr}T_{r}2\text{Al}_{20}$ ($Tr = \text{Ti, V}$) are such candidate systems and have the cubic CeCr$_2$Al$_{20}$-type crystal structure, as shown in Fig. 1 with the space group $Fd\bar{3}m$. The symmetry of $R$ site is $T_d$ and cubic [6]. Strong hybridization between $4f$ and $c$ electrons is expected because $R$
Figure 1. Crystal structure of Pr$_2$Al$_{20}$. The yellow, pink and aqua bolls represent Pr, transitional metal and Al respectively.

ions are surrounded by sixteen Al ions, which is the largest coordination number for tetrahedral groupings of spheres[7], indicating a large number of channels of hybridization.

Our previous report of Pr$_2$Al$_{20}$ revealed that [8]: (1) The CEF ground state of both Pr$_2$Al$_{20}$ and Pr$_2$Al$_{20}$ is the nonmagnetic $T_3$ ground doublet and well isolated from the first excited state by the gap of about 40 to 50 K. (2) Both materials exhibit quadrupolar order at $T_O = 2.0 K$ (Ti) and 0.6 K (V). (3) Both materials show strong hybridization effects including the conventional Kondo effects. The $-\ln T$ increase of the resistivity and large Weiss temperature of the susceptibility indicate the Kondo effect, which is found stronger in Pr$_2$Al$_{20}$ than the Ti counterpart. (4) Pr$_2$Al$_{20}$ exhibits anomalous metallic behavior such as divergent $C_P/T \sim T^{-3/2}$, $-T^{1/2}$ dependent Van Vleck susceptibility, and $T^{1/2}$ dependent resistivity over a decade of temperature between 2 and 20 K above $T_O = 0.6 K$. (5) All the above observations suggest that the increase in Kondo coupling by changing the Tr site from Ti to V suppresses the quadrupolar ordering, and instead leads to stronger hybridization between the quadrupoles of ground state and conduction electrons, and thus the quadrupolar Kondo effect.

Here, we report the results of the specific heat measurements of Pr$_2$Al$_{20}$ performed under $\mu_0 H = 0$ and 5 T // [111]. A large Sommerfeld coefficient $\gamma \sim 100$ (mJ/mole K$^2$) is observed above $T_O$ for Pr$_2$Al$_{20}$, which suggests the formation of heavy fermions.

2. Experimental
Single crystals of $RT_2$Al$_{20}$ ($R =$ Pr and La, $Tr =$Ti and V) were grown by an Al self-flux method under vacuum, using 4N(99.99%)-Pr, 3N-La, 3N-Ti,V and 5N-Al. The crystal structure was verified by the X-ray powder and single crystal diffraction measurements at room temperature and is found to have the lattice parameters $a = 14.723(7)$ Å (Ti) and 14.591(2) Å (V).
specific heat $C_P$ above 0.4 K were measured by a standard relaxation method.

3. Results and Discussion
Figure 2(a) shows the temperature dependence of the specific heat $C_P(T)$ of PrTi$_2$Al$_{20}$ (filled square), PrV$_2$Al$_{20}$ (filled circle), LaTi$_2$Al$_{20}$ (open square) and LaV$_2$Al$_{20}$ (open circle) under zero field. A peak indicated by an arrow is observed at $T_O=2.0$ K for PrTi$_2$Al$_{20}$ and 0.6 K for PrV$_2$Al$_{20}$, indicating the second order phase transition. As we discussed in [8], the CEF ground state of both PrTi$_2$Al$_{20}$ and PrV$_2$Al$_{20}$ is the nonmagnetic $\Gamma_3$ doublet. Besides, the first excited CEF state is located at $\Delta \approx 55$ K (Ti) and $\sim 40$ K (V), which is one order of magnitude larger than $T_O$. Therefore, these peaks do not come from a magnetic order but from a multipole order.

The inset of Fig. 2(a) shows the temperature dependence of the 4f electron contribution to the specific heat divided by temperature $C_{AF}/T$ of PrTi$_2$Al$_{20}$ (open square) and PrV$_2$Al$_{20}$ (open circle). This is determined by subtracting $C_P$ of the La analogs. For PrTi$_2$Al$_{20}$, $C_{AF}/T$ remains $\sim 100$ (mJ/mole K$^2$) above $T_O$ up to $\sim 10$ K. Note that in PrTi$_2$Al$_{20}$ the Fermi liquid behavior is observed in the temperature dependence of the resistivity in the same $T$ range above $T_O$ up to 20 K, namely, $\rho(T) \propto T^2$ [8]. The $T^2$ coefficient is estimated to be $A \sim 3.3$ ($\mu\Omega$cm/K$^2$). Therefore, the constant $C_{AF}/T \sim 100$ (mJ/mole K$^2$) should provide the estimate for the Sommerfeld coefficient, and as the result, the Kadowaki-Woods ratio is given by $A/\gamma^2 \sim 3.3 \times 10^{-6}$ ($\mu\Omega$cmK$^{-2}$/mJK$^{-2}$mole$^{-1}$)$^2$). Interestingly, this is close to the universal value known for heavy fermion systems [9]. Because the temperature range is much lower than the CEF gap scale, the large Sommerfeld coefficient should come from the mass enhancement.

![Figure 2](image-url)
due to the scattering process of conduction electrons by quadrupole moments, not by magnetic moments. In contrast, $C_{4f}/T$ of PrV$_2$Al$_{20}$ above $T_O$ is found to be strongly $T$ dependent and divergent down to $T_O$. The solid line in Fig. 2(a) inset shows the fit to the power law, namely $C_{4f}/T \propto T^{-\alpha}$ with $\alpha = 1.5$. As we discussed in detail in [8], this dramatic increase of $C_{4f}/T$ is attributable to the quadrupolar Kondo effect.

Figures 2(b) and (c) show $C_P$ under zero field (open circle) and $\mu_0H = 5$ T // [111] (filled diamond) at low temperatures of PrTi$_2$Al$_{20}$ and PrV$_2$Al$_{20}$, respectively. Unlike the $C_P$ under $\mu_0H // [100]$ (Fig. 3(a) and (b) in [8]), the peak temperature and the shape of $C_P$ under $\mu_0H // [111]$ for both PrTi$_2$Al$_{20}$ and PrV$_2$Al$_{20}$ show almost no change from the zero field results. This anisotropy and field insensitivity are the signatures of multipole ordering.

4. Conclusions
We have measured the specific heat of PrTr$_2$Al$_{20}$ and LaTr$_2$Al$_{20}$ (Tr = Ti, V) under $\mu_0H = 0$ and 5 T // [111]. Sharp peaks are observed owing to the quadrupole ordering at $T_O = 2.0$ K (Ti) and 0.6 K (V). In PrTi$_2$Al$_{20}$, a large $\gamma \sim 100$ (mJ/mole K$^2$) and large $\lambda$ coefficient observed above $T_O$ indicate the formation of heavy fermions due to the scattering process of conduction electrons by quadrupole moments. Field insensitive peak shape of $C_P$ for both PrTi$_2$Al$_{20}$ and PrV$_2$Al$_{20}$ supports the quadrupolar origin of the phase transition.

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6. References
[1] Cox D L 1987 Phys. Rev. Lett. 59 1240–1243
[2] Cox D L and Zawadowski A 1998 Adv. Phys. 47 599–942
[3] Yatskar A, Beyermann W P, Movshovich R and Canfield P C 1996 Phys. Rev. Lett. 77 3637–3640
[4] Tanida H, Suzuki H S, Takagi S, Onodera H and Tanigaki K 2006 J. Phys. Soc. Jpn. 75 073705
[5] Morin P, Schmitt D and du Tremolet de Lacheisserie E 1982 J. Magn. Magn. Mater. 30 257 – 264
[6] Niemann S and Jeitschko W 1995 J. Solid State Chem. 114 337–341
[7] Frank F C and Kasper J S 1958 Acta Cryst. 11 184–190
[8] Sakai A and Nakatsuji S 2011 J. Phys. Soc. Jpn. 80 063701
[9] Kadowaki K and Woods S 1986 Solid State Commun. 58 507 – 509