

# Effect of Ga Substitution on the $\Gamma_3$ Doublet Ground State in $\text{PrIr}_2\text{Zn}_{20}$

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**Abstract.** Electrical resistivity  $\rho$ , specific heat  $C$ , and magnetic susceptibility  $\chi$  measurements are reported on  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0.5$  and  $1.0$ . On cooling,  $\rho(T)$ 's monotonically decrease to the residual values which are two orders of magnitudes larger than that of  $\text{PrIr}_2\text{Zn}_{20}$ . A broad hump in  $C_m(T)$ 's at around 10 K can be reproduced by the two-level model with the  $\Gamma_3$  doublet ground state and the  $\Gamma_4$  triplet excited state. The magnetic entropy release shifts to higher temperatures with increasing  $x$ . The increase in  $\chi(T)$  at  $T < 5$  K contrasts with the saturation of  $\chi(T)$  for  $x=0$ . These observations indicate the splitting of the ground state doublet due to the lowering of the local symmetry at the Pr site by the Ga substitution.

## 1. Introduction

Praseodymium-based cubic compounds with  $4f^2$  configuration attract much attention because they show various phenomena arising from (quasi-)degenerated ground states. In a Pr-filled skutterudite  $\text{PrOs}_4\text{Sb}_{12}$ , the feasibility of superconductivity mediated by quadrupolar fluctuations has been pointed out by the measurements of neutron scattering and nuclear quadrupole resonance [1, 2, 3]. A well-known example of a  $4f^2$  cubic system is  $\text{PrPb}_3$  with the  $\text{AuCu}_3$ -type structure, where the cubic crystalline electric field (CEF) splits the ninefold multiplet of  $J = 4$  into four multiplets. The CEF ground state of the  $\Gamma_3$  doublet carries no magnetic dipole moment but electric quadrupoles. Thereby, the low temperature property is governed by the interaction of the quadrupoles and the conduction electrons. In fact,  $\text{PrPb}_3$  undergoes an antiferroquadrupole (AFQ) transition at  $T_Q = 0.4$  K [4]. The combined analysis of magnetization and neutron diffraction experiments identified the AFQ order parameter as the quadrupole  $O_2^0$  [5, 6]. The quadrupole moments are aligned with an incommensurate sinusoidally modulated structure even in the ground state. Thereby, the indirect RKKY-type interaction between the quadrupoles plays the essential role. On the other hand, substituting La for Pr in  $\text{PrPb}_3$  destroys the AFQ order at a small amount of  $x = 0.03$  in  $\text{Pr}_{1-x}\text{La}_x\text{Pb}_3$  [7]. For  $x \geq 0.95$ , on the other hand, there appears non-Fermi liquid (NFL) behavior. Because the electric quadrupole conserves the time-reversal symmetry, it has two orbital channels. If the localized quadrupole is overcompensated by the conduction electrons, the following NFL behaviors would



appear; the magnetic susceptibility  $\chi \sim \ln T$ , specific heat  $C/T \sim \ln T$  and electrical resistivity  $\rho - \rho_0 \propto 1 + A\sqrt{T}$ , where  $\rho_0$  is residual resistivity and  $A$  is a coefficient [8]. More important is the residual entropy of  $(1/2)R\ln 2$  at zero temperature. The absence of AFQ order in  $\text{PrAg}_2\text{In}$  [9] and  $\text{PrMg}_3$  [10, 11] with the  $\Gamma_3$  doublets ground state has been discussed by taking the chemical disorder effect into consideration.

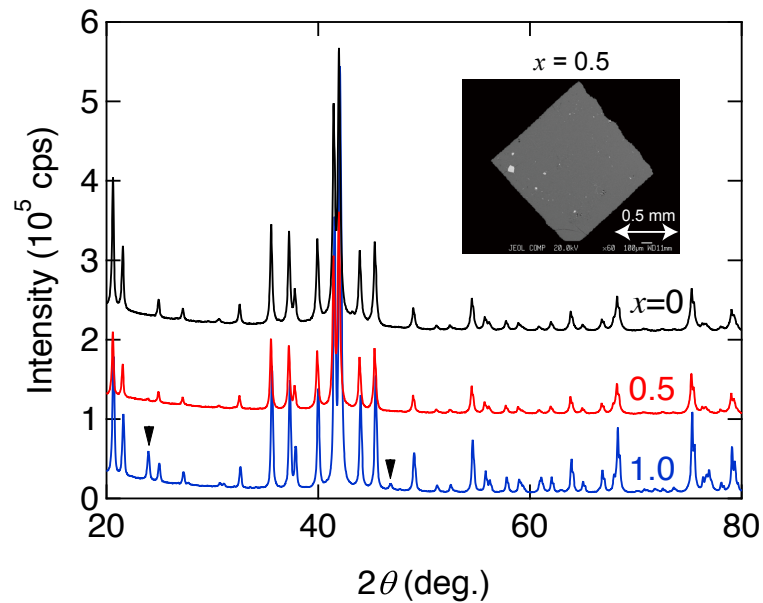
Recently, much attentions are drawn to a family of a cubic system  $\text{PrT}_2\text{X}_{20}$  ( $X=\text{Al}$  and  $\text{Zn}$ ) which show a variety of phenomena such as quadrupole order, heavy-fermion superconductivity, and structural transitions [12, 13, 14]. The CEF ground state of most compounds is the non-Kramers  $\Gamma_3$  doublet possessing no magnetic dipoles but electric quadrupoles [15, 16]. Among them,  $\text{PrIr}_2\text{Zn}_{20}$  undergoes an AFQ order at  $T_Q=0.11$  K and a superconducting transition at  $T_c=0.05$  K, suggesting a possible contribution of the quadrupole fluctuations to the superconducting Cooper-pair formation [12, 13]. The coexistence of the AFQ order and the superconducting state has been also observed in the isostructural  $\text{PrRh}_2\text{Zn}_{20}$ ,  $\text{PrTi}_2\text{Al}_{20}$ , and  $\text{PrV}_2\text{Al}_{20}$  [17, 18, 19]. In  $\text{PrTi}_2\text{Al}_{20}$ ,  $T_c=0.2$  K at ambient pressure is enhanced up to 1 K under high pressure, for which a quantum critical phenomenon due to the quadrupolar degrees of freedom has been proposed [20]. On the other hand, in  $\text{PrIr}_2\text{Zn}_{20}$ , in the temperature range  $0.2 < T < 0.8$  K, above  $T_Q$ , the magnetic specific heat  $C_m$  and  $\rho(T)$  exhibit NFL behavior;  $C_m/T$  and  $\rho$  are proportional to  $-\ln T$  and  $\sqrt{T}$ , respectively [21]. All data set of  $C_m$  and  $\rho(T)$  in magnetic fields  $B \leq 6$  T are well scaled with characteristic temperature  $T_0$ . Because the constituent atoms are ordered periodically in the high quality crystal with low residual resistivity of  $0.2 \mu\Omega \text{ cm}$ , these temperature variations of  $C_m$  and  $\rho$  strongly suggest the formation of a quadrupole Kondo lattice, in which quadrupole moments are periodically placed and overcompensated by the conduction electrons, leading to the NFL state with an energy scale of  $k_B T_0$  [21, 22].

In the present work, the effects of the Ga substitution on the ground state of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0.5$  and  $1.0$  were studied by the  $\rho(T)$ ,  $C(T)$ , and  $\chi(T)$  measurements. Since the electronic number of Ga is one more than that of Zn, it is expected that hybridization between the  $4f$  and conduction electrons could be enhanced by the increase of  $4p$  electron density due to the Ga substitution for Zn, and the NFL behavior would be modified.

## 2. Experimental

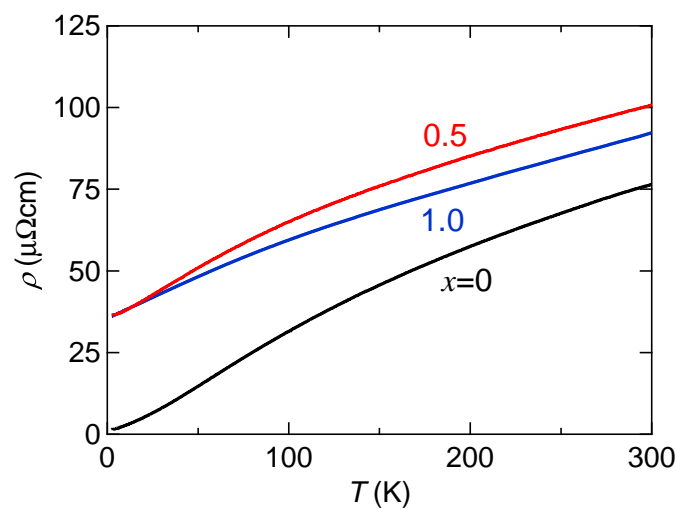
Single crystalline samples of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  were synthesized by the melt-growth method from the high-purity elements Pr (4N), Ir (3N), Zn (6N), and Ga (6N). The details of sample preparation were reported in the previous paper [12].

The samples were characterized by the X-ray powder diffraction technique and electron-probe microanalysis (EPMA). The X-ray diffraction patterns with using the  $\text{Cu } K_\alpha$  radiation for  $x=0$ ,  $0.5$  and  $1.0$  are shown in Fig. 1. Almost all of the peaks can be indexed by the cubic  $\text{CeCr}_2\text{Al}_{20}$ -type structure [23], although some impurity peaks are found in the pattern for  $x=1.0$  as depicted with the arrows in Fig. 1. The inset of Fig. 1 shows the backscattered electron image for  $x=0.5$ . There are small amounts of secondary phases in addition to the main phases. The atomic compositions were determined by the EPMA using an electron beam of 20 keV on a JEOL JXA-8200 analyzer. The crystal compositions of the main phases were determined as  $\text{PrIr}_{1.9(1)}\text{Zn}_{19.4(2)}\text{Ga}_{0.49(2)}$  and  $\text{PrIr}_{1.9(1)}\text{Zn}_{18.9(5)}\text{Ga}_{1.0(1)}$  for  $x=0.5$  and  $1.0$ , respectively, by averaging over 10 different regions for each crystal, where it was assumed that the Pr sites are fully occupied. The crystal compositions of Ga equal the starting ones. The results confirmed the chemical homogeneity of the samples used for the measurements of physical properties. The solid solubility limit was found to be  $x=1.3$ . The secondary phase for the  $x=0.5$  sample is  $\text{PrIr}_{4.6}\text{Zn}_{15.4}\text{Ga}_{2.7}$ . On the other hand, that for  $x=1.0$  is a nonmagnetic  $\text{Ir}(\text{Zn},\text{Ga})_{5.9}$ . The lattice parameters were determined by the Rietveld refinement of the X-ray diffraction patterns using the program RIETAN-FP [24]. The lattice parameter for  $x=1.0$  decreases by only 0.1% from that for  $x=0$ .

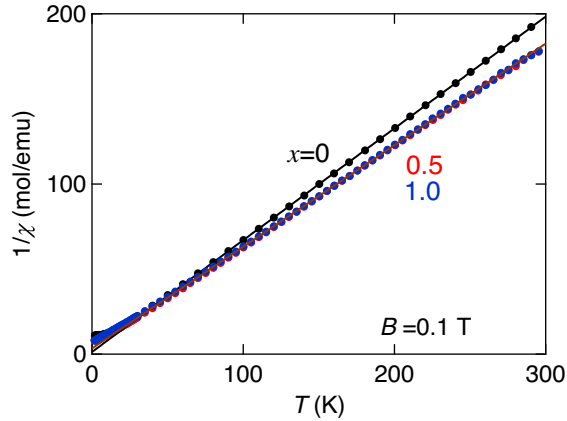


**Figure 1.** Powder X-ray diffraction patterns of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0, 0.5$  and  $1.0$ . The data are offset for clarity. The arrows indicate the peaks due to an impurity phase. The inset shows the backscattering electron image of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0.5$ .

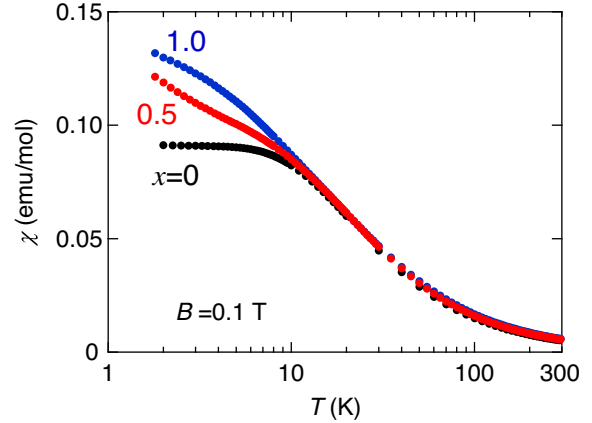
The electrical resistivity  $\rho$  was measured by a standard four-probe AC method using a laboratory built system. A Gifford-McMahon type refrigerator was used in the temperature range for  $3 \leq T \leq 300$  K. The specific heat  $C$  between 0.4 and 20 K was measured by a thermal relaxation method using a Quantum Design physical property measurement system. Magnetic susceptibility  $\chi$  was measured using a commercial SQUID magnetometer (Quantum



**Figure 2.** Temperature dependence of the electrical resistivity of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0, 0.5$ , and  $1.0$ .



**Figure 3.** Temperature dependence of the magnetic susceptibility of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0$  [12], 0.5, and 1.0 measured in the magnetic field of  $B=0.1$  T.



**Figure 4.** Temperature dependence of the magnetic susceptibility of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0$  [12], 0.5, and 1.0 measured in the magnetic field of  $B=0.1$  T.

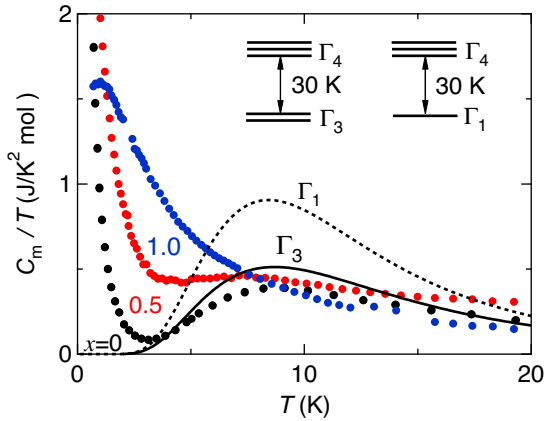
Design MPMS) between 1.8 and 300 K.

### 3. Results and discussion

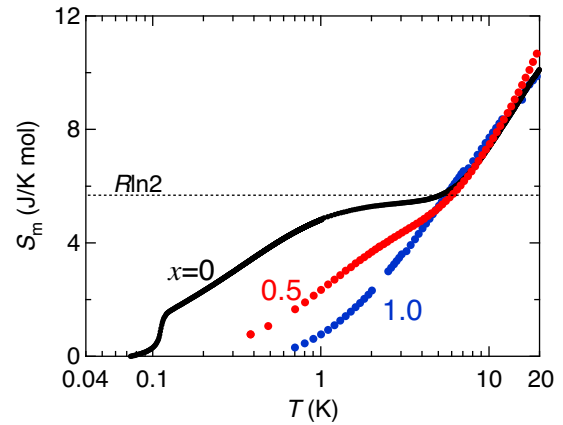
The temperature dependence of the electrical resistivity  $\rho(T)$  of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0, 0.5$  and  $1.0$  are shown in Fig. 2. On cooling,  $\rho(T)$  monotonically decreases with an upward curvature. The values of residual resistivity for  $x=0.5$  and  $1.0$  are  $36 \mu\Omega \text{ cm}$ , whose values are two orders of magnitudes larger than that for  $x=0$ . The values of the residual resistivity ratio (RRR) defined as  $\rho(300\text{K})/\rho(2\text{K})$  for  $x=0.5$  and  $1.0$  are 2.8 and 2.6, respectively. The decrease of RRR by the Ga substitution probably results from the atomic disorder due to the Ga substitution, which prevents us from detecting a change of the  $\sqrt{T}$  dependence of  $\rho(T)$  observed for  $x=0$ .

Figure 3 shows the temperature dependence of the inverse magnetic susceptibility  $\chi^{-1}(T)$  for  $x=0$  [12], 0.5 and 1.0 measured in a field of  $B=0.1$  T. Above 20 K,  $\chi^{-1}(T)$ 's for  $x=0.5$  and 1.0 are linear in  $T$  as is expected from the Curie-Weiss law. The effective magnetic moments of  $\mu_{\text{eff}} = 3.66 \mu_B/\text{Pr-ion}$  for  $x=0.5$  and 1.0 are close to  $3.49 \mu_B/\text{Pr-ion}$  for  $x=0$ . The paramagnetic Curie temperatures  $\theta_p$ 's for  $x=0.5$  and 1.0 are  $-5.2$  and  $-5.6$  K, respectively, indicating that the intersite magnetic interactions between the magnetic moments of CEF excited states of the trivalent Pr ions are weakly antiferromagnetic. Figure 4 shows  $\chi(T)$  of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  measured in a magnetic field of  $B=0.1$  T. As  $T$  goes down to 2 K,  $\chi(T)$ 's for  $x=0.5$  and 1.0 continue to increase, although that for  $x=0$  is saturated below 5 K [12]. The origin of the increment of  $\chi(T)$  at  $T < 5$  K for  $x=0.5$  and 1.0 will be discussed later.

We turn our attention to the change in the specific heat by the Ga substitution. Figure 5 shows the temperature dependence of the magnetic specific heat divided by temperature  $C_m/T$  for  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  with  $x=0$  [13], 0.5, and 1.0. The values of  $C_m$  for  $x=0.5$  and 1.0 were estimated by subtracting the specific heat of  $\text{LaIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0.5$  and 1.0, respectively, as the lattice and conduction electron contributions from those of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$ . For  $x=0$ , the broad peak appears at around 10 K as was previously reported, which was reproduced by the  $\Gamma_3$  doublet -  $\Gamma_4$  triplet two-level model with an energy split of 30 K, as shown with the solid curve [13]. For  $x=0.5$ , the peak is much broadened than that for  $x=0$ . The magnitude at  $T > 7$  K is comparable to the calculation for the  $\Gamma_3$  doublet ground state rather than that for the  $\Gamma_1$  singlet ground state shown with the dashed curve in Fig. 5. For  $x=1.0$ ,  $C_m/T$  is monotonically increases on cooling. The magnitude of  $C_m/T$  for  $T > 7$  K is more comparable



**Figure 5.** Temperature dependence of the specific heat of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0$  [13], 0.5, and 1.0. The solid and dashed curves are calculations using two-level models with the  $\Gamma_3$  doublet and the  $\Gamma_1$  singlet ground states, respectively, as shown in the inset.



**Figure 6.** Temperature variation of the magnetic entropy  $S_m$  of  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0$  [13], 0.5, and 1.0, which are estimated by integrating  $C_m/T$  with respect to the temperature. It was assumed that  $S_m$  reaches  $R\ln 2$  at 5 K.

to the calculation of the two-level model with the  $\Gamma_3$  doublet ground state than that with the  $\Gamma_1$  singlet ground state. Considering the moderate agreement between the experimental data and the calculation for  $T > 7$  K, we expect that the CEF ground state of the  $\text{Pr}^{3+}$  ion in the Ga substitution system would remain in the  $\Gamma_3$  doublet as in  $\text{PrIr}_2\text{Zn}_{20}$ . Note that  $C_m/T$ 's for  $x=0.5$  and 1.0 at  $T < 7$  K diverge upward from the two-level model calculation with the  $\Gamma_3$  doublet ground state. This divergence suggests that the doubly degenerated state is split by the Ga substitution. With respect to the NFL behavior for the specific heat, the  $-\ln T$  dependence of  $C_m/T$  observed in  $\text{PrIr}_2\text{Zn}_{20}$  vanishes for  $x=1.0$ , and instead,  $C_m/T$  shows a broad peak at around 1 K, indicating collapse of the NFL state.

The magnetic entropy  $S_m$  for  $x=0.5$  and 1.0 estimated by integrating  $C_m/T$  with respect to the temperature is shown in Fig. 6. Here, it was assumed that  $S_m$ 's commonly reach  $R\ln 2$  at 5 K. The curve of  $S_m(T)$  shifts to higher temperatures with increasing  $x$ , indicating that the entropy of  $R\ln 2$  due to the two-fold degeneracy of the  $\Gamma_3$  doublet is removed at higher temperature. It is reasonable because  $C_m/T$ 's for  $x=0.5$  and 1.0 diverge from the two-level model calculation at  $T < 7$  K as mentioned above.

Let us discuss possible mechanisms for the enhancement of  $\chi(T)$  at  $T < 5$  K and the release of the magnetic entropy at the higher temperatures in the Ga substituted system. One is the enhancement of the hybridization between the  $4f$  and conduction electrons due to the increase of  $4p$  electron density. Recently, emergence of a Fermi liquid state accompanied with a free magnetic spin in the vicinity of the non-Fermi liquid state has been theoretically pointed out for Pr-based compounds with the  $\Gamma_3$  doublet ground state, where competition between the magnetic and quadrupole Kondo effects was considered on the basis of an extended two-channel Kondo model.[25] If this is the case,  $\chi(T)$  could be enhanced compared with that for  $x=0$ . In addition, if the NFL state would collapse by the Ga substitution, then the characteristic temperature shifts to higher temperatures and the magnetic entropy is released at the higher temperatures.

However, it is elusive whether the hybridization could be strengthened by the small amount of the substitution for  $x \leq 1.0$ . More plausible mechanism is the lowering of local symmetry at the Pr site by the atomic disorder. In this case, the  $\Gamma_3$  doublet is split into two singlets, whose energy is statistically distributed. Thereby, the magnetic entropy is released at higher temperatures.

Furthermore,  $\chi(T)$  is increased on cooling until the thermal population of the upper singlet becomes negligible. If the splitting energy is less than 1 K, then  $\chi(T)$  would continuously increase down to 2 K. The splitting of the doublet ground state probably makes the two-channel orbitals anisotropic. By the channel anisotropy, emergence of a crossover from NFL to FL state was theoretically proposed.[26] In any events, the NFL state in  $\text{PrIr}_2\text{Zn}_{20}$  arising from the formation of the quadrupole Kondo lattice becomes unstable by the Ga substitution. To reveal the ground state of the Ga substituted system, further measurements at lower temperatures below 0.4 K are on going.

#### 4. Conclusion

The transport and magnetic properties of Ga substituted system  $\text{PrIr}_2\text{Zn}_{20-x}\text{Ga}_x$  for  $x=0.5$  and 1.0 were studied by the measurements of the  $\rho(T)$ ,  $C_m(T)$ , and  $\chi(T)$ .  $\rho(T)$  monotonically decreases on cooling. The high residual resistivity is attributed to the atomic disorder. The hump in  $C_m(T)/T$  at around 10 K can be moderately reproduced by the two-level model with the  $\Gamma_3$  doublet ground state. The release of the magnetic entropy estimated from  $C_m$  shifts to higher temperatures.  $\chi(T)$  increases on cooling at  $T < 5$  K, which is in contrast to the saturation behavior for  $x=0$ . These observations indicate the splitting of the ground state doublet due to lowering of the local symmetry at the Pr site by the Ga substitution.

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#### References

- [1] Bauer E D, Frederick N A, Ho P C, Zapf V S and Maple M B 2002 *Phys. Rev. B* **65** 100506
- [2] Kuwahara K, Iwasa K, Kohgi M, Kaneko K, Metoki N, Raymond S, Méasson M -A, Flouquet J, Sugawara H, Aoki Y and Sato H 2005 *Phys. Rev. Lett.* **95** 107003
- [3] Yogi M, Nagai T, Imamura Y, Mukuda H, Kitaoka Y, Kikuchi D, Sugawara H, Aoki Y, Sato H and Harima H 2006 *J. Phys. Soc. Jpn.* **75** 124702
- [4] Tayama T, Sakakibara T, Kitami K, Yokoyama M, Tenya K, Amitsuka H, Aoki D, Ōnuki Y and Kletowski Z 2001 *J. Phys. Soc. Jpn.* **70** 248
- [5] Onimaru T, Sakakibara T, Harita A, Tayama T, Aoki D and Ōnuki Y 2004 *J. Phys. Soc. Jpn.* **73** 2377
- [6] Onimaru T, Sakakibara T, Aso N, Yoshizawa H, Suzuki H S and Takeuchi T 2005 *Phys. Rev. Lett.* **94** 197201
- [7] Kawae T, Kinoshita K, Nakaie Y, Tateiwa N, Takeda K, Suzuki H S and Kitai T 2006 *Phys. Rev. Lett.* **96** 027210
- [8] Cox D L and Zawadowski Z 1998 *Adv. Phys.* **47** 599
- [9] Yatskar A, Beyermann W P, Movshovich R and Canfield P C 1996 *Phys. Rev. Lett.* **77** 3637
- [10] Tanida H, Suzuki H S, Takagi S, Onodera H and Tanigaki K 2006 *J. Phys. Soc. Jpn.* **75** 073705
- [11] Morie T, Sakakibara T, Suzuki H S, Tanida H and Takagi S 2009 *J. Phys. Soc. Jpn.* **78** 033705
- [12] Onimaru T, Matsumoto K T, Inoue Y F, Umeo K, Saiga Y, Matsushita Y, Tamura R, Nishimoto K, Ishii I, Suzuki T and Takabatake T 2010 *J. Phys. Soc. Jpn.* **79** 033704
- [13] Onimaru T, Matsumoto K T, Inoue Y F, Umeo K, Sakakibara T, Karaki Y, Kubota M and Takabatake T 2011 *Phys. Rev. Lett.* **106** 177001
- [14] Sakai A and Nakatsuji S 2011 *J. Phys. Soc. Jpn.* **80** 063701
- [15] Iwasa K, Kobayashi H, Onimaru T, Matsumoto K T, Nagasawa N, Takabatake T, Ohira-Kawamura S, Kikuchi T, Inamura Y and Nakajima K 2013 *J. Phys. Soc. Jpn.* **82** 043707
- [16] Sato T J, Ibuka S, Nambu Y, Yamazaki T, Hong T, Sakai A and Nakatsuji S 2012 *Phys. Rev. B* **86** 184419
- [17] Onimaru T, Nagasawa N, Matsumoto K T, Wakiya K, Umeo K, Kittaka S, Sakakibara T, Matsushita Y and Takabatake T 2012 *Phys. Rev. B* **86** 184426

- [18] Sakai A, Kuga K and Nakatsuji S 2012 *J. Phys. Soc. Jpn.* **81** 083702
- [19] Tsujimoto M, Matsumoto Y, Tomita T, Sakai A and Nakatsuji S 2014 *Phys. Rev. Lett.* **113** 267001
- [20] Matsubayashi K, Tanaka T, Sakai A, Nakatsuji S, Kubo Y and Uwatoko Y 2012 *Phys. Rev. Lett.* **109** 187004
- [21] Onimaru T *et al.* unpublished
- [22] Tsuruta A and Miyake K 2015 *J. Phys. Soc. Jpn.* **84** 114714
- [23] Nasch T, Jeitschko W and Rodewald U C 1997 *Z. Naturforsch. B* **52** 1023
- [24] Izumi F and Momma K 2007 *Solid State Phenom.* **130** 15
- [25] Kusunose H and Onimaru T 2015 *J. Phys.: Conf. Ser.* **592** 012099
- [26] Yotsuhashi S and Maebashi H 2002 *J. Phys. Soc. Jpn.* **71** 1705