Critical behavior in a Kondo-screening partially-ordered antiferromagnet CePdAl

Akira Oyamada¹, Tomomi Kaibuchi¹, Masahide Nishiyama¹, Tetsuaki Itou¹, Satoru Maegawa¹, Yosikazu Isikawa², Andreas Dönni³, and Hideaki Kitazawa³
¹Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, JAPAN
²Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, JAPAN
³National Institute for Materials Science, Tsukuba 305-0047, JAPAN
E-mail: oyamada.akira.2s@kyoto-u.ac.jp

Abstract. A rare-earth compound CePdAl is a good example of the Kondo-screening partially-ordered antiferromagnet below $T_N = 2.7$ K. In this compound, the formation of the Kondo-singlet state is realized as a new route of the relief of the frustration. The spin dynamics of CePdAl are, however, still controversial. In order to further investigate the spin dynamics of CePdAl, we have performed $^{27}$Al-NMR and specific heat single crystal measurements and reanalysed published powder neutron diffraction data. NMR intensities decrease with decreasing temperature in the ordered state suggesting the slow spin fluctuations below $T_N = 2.7$ K, while the intensity of magnetic Bragg peak measured by neutron diffraction increases monotonously in the same temperature range. The critical exponents derived from the neutron diffraction and the specific heat measurements are not coincident with those of known universality classes. An unconventional magnetic order parameter or a charge degree of freedom originated from the coexistence of frustration and the Kondo effect may influence the critical behavior.

1. Introduction
The interplay between the Kondo effect and the geometrical frustration is one of the most attractive issues [1]. The competition between RKKY interactions and the Kondo effect are often observed in f-electron compounds with the magnetic ions of Ce, Sm, Eu, Yb and U. The RKKY interactions are the origin of magnetic orderings, while the Kondo effect tends to quench the magnetic moments and competes with the magnetic orderings. This competition results in a quantum critical point (QCP) at the boundary between a non-magnetic heavy-fermion state and a magnetically ordered state. Anomalous phenomena like non-Fermi-liquid state around QCP attract much attention. On the other hand, the geometrical frustration prevents the usual magnetic orderings and often cause a disordered state or a peculiar magnetic ordered state. Furthermore new universality class may be originated by the frustration, for example in XY stacked triangular antiferromagnet [2]. If the RKKY interactions, the Kondo effect and the geometrical frustration coexist, a new quantum state may be originated.

A Kondo-screening partially-ordered state is one example of an attractive quantum state. A part of the magnetic moments are ordered below the transition temperature and the others
Figure 1. Projection onto the c-plane of the crystal and magnetic structure of CePdAl. The symbols +, −, and 0 show up spin, down spin and disordered spin, respectively.

are disordered. Although the partially-ordered state has been observed in localized spin system with the frustration and the Ising-type anisotropy [5], the partially-ordered state in Kondo lattice is a different quantum state. The disordered moments remained in the ordered state are not paramagnetic but in the Kondo singlet state.

A rare-earth compound CePdAl is a Kondo-screening partially-ordered antiferromagnet as shown in figure 1. In CePdAl, two thirds of magnetic moments are in the ordered state with sine wave structure along the c-axis below $T_N = 2.7$ K and a third of moments are disordered [4]. NMR measurements have shown that the disordered moments are in the Kondo singlet state [5]. This situation brings a new route of relief from the frustration to light. The frustration is relieved by the disappearance of one third of moments due to the formation of the Kondo singlet state and the partially-ordered state is stabilized down to 0 K.

The crystal structure of CePdAl is hexagonal ZrNiAl-type as shown in figure 1 and its space group is $P\bar{6}2m$ [6]. The magnetic Ce$^{3+}$ ions are on the network of the regular triangles in the c-plane. The network is similar to the Kagome lattice, however the hexagons are distorted. The distance between the nearest neighbor Ce atoms are considerably shorter in the c-plane than in the c-axis, suggesting the strong two-dimensional magnetic correlations. The degeneracy of the total spin $J = 5/2$ of Ce$^{3+}$ lifts to three doublets in the crystal field. The ground state doublet is regarded as the effective spin $1/2$ with a strong Ising-type anisotropy [7].

Neutron diffraction measurements of powder samples have revealed that the Ce moments order antiferromagnetically below 2.7 K ($T_N$) with a propagating vector $k = [1/2, 0, \tau]$, $\tau \approx 0.35$, as shown in Fig. 1 [4]. The magnetic structure is partially ordered in the c-
plane and incommensurate sine waves along the c-axis. The magnetic structure of this partially ordered state in CePdAl was explained by a two-dimensional mean field approximation including the Kondo effect [8], however, the spin dynamics of CePdAl are still controversial. The most remarkable feature of the spin dynamics is an anomalous temperature dependence of the NMR relaxation rate \( T_1^{-1} \). The rate \( T_1^{-1} \) is proportional to \( \exp(\delta/T) \) with \( \delta = 2.7K \) between \( T_N = 2.7K \) and 50 K, which is similar to that of two dimensional Heisenberg system although CePdAl has strong Ising-type anisotropy [5].

In order to further investigate the spin dynamics of CePdAl, we have performed NMR and specific heat single crystal measurements and reanalysed published powder neutron diffraction data [4].

2. Experimental Procedures
Single crystals of CePdAl were prepared by Czochralski method. We performed \(^{27}\)Al-NMR measurements of a single crystal using a coherent spectrometer. The magnetic field is applied along the c-axis, that is one of the principal axes of the electric field gradient tensor. The operating frequency was 18.78 MHz. Spin echo spectra were measured by a field sweep. Specific heat measurements of a single crystal were performed using a thermal relaxation method between 2 and 10 K with Quantum Design PPMS.

3. Results and Discussions
Figure 2 shows the temperature variation of spin echo spectra of a single crystal above and below \( T_N \). The five peaks of the spectra come from the first order quadrupolar effect for \( I = 5/2 \) of \(^{27}\)Al nuclei. The intensity of the spectra starts to decrease above \( T_N \) significantly and disappears below 2.8 K without remarkable broadening.

Figure 3 shows the temperature dependence of the integrated spin echo intensity of a single crystal. The integrated intensity of powder samples are also plotted for comparison [14]. The effects of the temperature and spin-spin relaxation time \( T_2 \) have been corrected. The temperature dependence of \( T_2 \) is rather weak and has only a small increase around \( T_N \). The spectra of the powder samples at lowest temperature consists of seven peaks and is in the field range of Fig.5 [5]. Thus the intensity is proportional to the number of detected nuclei. The integrated intensity considerably decreases below 3.5 K although no temperature dependence is expected. However, the intensity of powder samples recovers below 2 K while the intensity of a single crystal is completely lost below 2.5 K. Here we have to note that the compound is a metallic system. In general, the intensity decreases with decreasing of the resistivity due to the skin effect. However, the resistivity decreases below \( T_N \) while the integrated intensity decreases below 3.5 K, that is significantly higher than \( T_N = 2.7K \). Furthermore since the change of the resistivity is small [15, 16], the skin effect has only slight effect on the intensity. Thus the anomalous decrease and the difference between a single crystal and powder samples are intrinsic. This decrease of the intensity means the decrease of number of detected nuclei and can be explained as follows. The relaxation time \( T_2 \) in a part of the sample becomes much shorter than \( \sim 10 \) \( \mu s \) and NMR can not detect the part of the sample. While \( T_2 \) is larger in the other part of the sample, NMR can detect the signal of the other part. This situation suggests that the slow spin fluctuation with the order of MHz frequency remains below \( T_N \) inhomogeneously. There is no definitive explanation of the slow spin fluctuation for the moment. We will discuss the slow spin fluctuation later.

On the other hand, the neutron diffraction measurements showed that the magnetic Bragg peak intensity increases with decreasing temperature monotonously in the temperature range where the NMR intensity decreases significantly [4]. In order to investigate whether the temperature dependence of the magnetic Bragg peak intensity is conventional or not, we have reanalyzed the neutron diffraction data [4] and estimated the critical exponent \( \beta \). A sublattice
Figure 2. Temperature variation of spin echo spectra of a single crystal above and below \( T_N \).

magnetization or the Fourier component of the magnetic structure obeys the relation, \( M \propto e^\beta \) below and close to \( T_N \), where \( \epsilon = (T_N - T)/T_N \). The Fourier component is proportional to the root of Bragg peak intensity. Figure 4 shows the Fourier component versus \( \epsilon \) plot. The solid line shows the best fit of the experimental data to a power law with \( T_N = 2.77 \) K. The value of \( \beta \) is estimated to be 0.22 \( \pm \) 0.02. There are two other reports on neutron diffraction experiments. One is using powder samples [9] and the other is using a single crystal [10]. Within the experimental error, our result is compatible with the \( \beta \) values estimated from these two experimental data. This value is considerably smaller than the usual values of three-dimensional (3D) Ising (0.33), 3D XY (0.35) and 3D Heisenberg model (0.37). Now we have to keep one point in mind. In CePdAl, the long range RKKY or dipolar interactions are important. Thus \( \beta \) may become close to the value derived from the mean field approximation or infinite range model, that is 0.5 [11, 12]. Therefore the smaller value obtained for \( \beta \) is quite anomalous.

Figure 5 shows the temperature dependence of the specific heat between 2 K and 10 K. A sharp peak was observed around 2.7 K that confirms the existence of the magnetic phase transition. The tail above 2.7 K shows that the development of the short range correlations is extending over wide temperature range. In order to estimate the critical exponent \( \alpha \) and \( \alpha' \), a single logarithmic plot of the specific heat against the |\( \epsilon \)| is shown in figure 6. This plot shows the critical behavior is extending to a rather large temperature range above \( T_N \) and it becomes difficult to distinguish between critical behavior and short range fluctuations. This means that \( \alpha \) above \( T_N \) was not estimated correctly. On the other hand, in the case of CePdAl the exchange interactions are thought to be dominated by long-range RKKY interactions. Therefore the true
Figure 4. Fourier component of the magnetic ordered structure versus the reduced temperature \((T_N - T)/T_N\). The solid line shows the best fit of the experimental data to a power law with \(T_N = 2.77\) K and \(\beta = 0.22\).

Figure 5. Temperature dependence of the specific heat between 2 K and 10 K.

Figure 6. Specific heat versus the reduced temperature plot.

critical region may be smaller than the measured \(\epsilon\) region and the estimation of the critical exponents may be difficult although the similarity to PdCrO$_2$ is remarkable.

As previously mentioned, there is no definitive explanation of the slow spin fluctuation below \(T_N\) and the unconventional critical exponents. Here we note that the magnetic structure in CePdAl is the incommensurate sine wave along the c-axis stabilized by the Kondo effect. If only the phase degree of freedom in the sine wave fluctuates, the local field which NMR observes fluctuates but the amplitude of the Fourier component orders. This explains the decrease of NMR intensity and the monotonous development of the Bragg peak observed by neutron diffraction measurements. Since the phase fluctuations are accompanied by the exchange of the spin-up sites and the spin-down sites in the c-plane, the phase fluctuations may be related with the frustration in the c-plane. If the defects in the crystal lock the phase fluctuations, the difference between powder samples and a single crystal may be explained as we expect the larger amount of
defects in the powder samples. This scenario also seems to relate with the unconventional $\beta$ and the temperature dependence of the k-vector. Similar decrease of the NMR intensity below $T_N$ was observed in the two-dimensional Heisenberg triangular antiferromagnets NaCrO$_2$, LiCrO$_2$ and NiGa$_2$S$_4$ [17, 18, 19]. In those compounds, the possibility of the spin fluctuations due to the excitations of $Z_2$ vortices was proposed. Since CePdAl has a strong Ising-type anisotropy and the Kondo effect, the origin of the slow spin fluctuation must be different from those materials. The interesting point is that the similar properties to those two-dimensional Heisenberg systems emerges in CePdAl due to the coexistence of the frustration and the Kondo effect.

Recently, variational Monte-Carlo simulations of the Kondo lattice model on the triangular lattice with Ising-type anisotropy have been reported [20]. In this theory, the charge disproportionation occurs in the partially ordered state. This result pose an interesting question that how the charge degree of freedom is involved in the magnetic phase transition. In CePdAl, both spin and charge degrees of freedom may also play important roles in the anomalous critical behavior.

In summary, the critical behavior of CePdAl was investigated by $^{27}$Al-NMR, neutron diffraction and specific heat measurements. The anomalous decrease of the NMR intensity was observed suggesting the slow spin fluctuation below $T_N$. While the Bragg peak observed by neutron diffraction measurements develops monotonously with decreasing temperature but with an unconventional $\beta$ value. The slow spin fluctuation and the unconventional critical exponents seems to be closely related with the coexistence of frustration and the Kondo effect.

Acknowledgments
This study was supported by a Grant-in-Aid for Scientific Research on Priority Areas ”Novel States of Matter Induced by Frustration” (19052005).

References
[1] Ballou R, Lacroix C and NunezRegueiro M D 1991 Phys. Rev. Lett. 66 1910
[2] Kawamura H 1986 J. Phys. Soc. Jpn. 55 2095
[3] T. Takagi and M. Mekata 1993 J. Phys. Soc. Jpn. 62 3943
[4] Dönni A, Ehlers G, Maletta H, Fischer P, Kitazawa H and Zolliker M 1996 J. Phys.: Condens. Matter 8 11213
[5] Oyamada A, Nishiyama M, Maegawa S, Kitazawa H and Isikawa Y 2008 Phys. Rev. B 77 064432
[6] Hulliger F 1995 J Alloys Compounds B 218 44
[7] Isikawa Y, Mizushima T, Fukushima N, Kuwai T, Sakurai J and Kitazawa H 1996 J. Phys. Soc. Jpn. 65 Suppl.B 117
[8] Dolores M, Regueiro N, Lacroix C, Canals B 1997 Physica C 282-287 1885
[9] Keller L, Dönni A, Kitazawa H and van den Brandt B 2002 Appl. Phys. A 74 S686
[10] Prokes K, Manuel P, Adroja D T, Kitazawa H, Goto T and Isikawa Y 2006 Physica B 385-386 359
[11] Kotzler J 1976 J. Phys. C: Solid State Phys. 9 1291
[12] Larkin A I and Khmelnitskii D E 1969 Sov. Phys. -JETP 29 1123
[13] Takatsu H, Yoshizawa H, Yonezawa S and Maeno Y 2009 Phys. Rev. B 79 104424
[14] Oyamada A, Kamioka K, Hashi K, Maegawa S, Goto T and Kitazawa H 1996 J. Phys. Soc. Jpn. 65 Suppl. B 123
[15] Kitazawa H, Matsushita A, Matsumoto T and Suzuki T 1994 Physica B 199-200 28
[16] Goto T, Hane S, Umeo K, Takabatake T and Isikawa Y 2002 J. Phys. Chem. Solids 63 1159
[17] Olariu A, Mendels P, Bert F, Ueland B G, Schiffer P, Berger R F and Cava R J 2006 Phys. Rev. Lett. 97 167203
[18] Alexander L K, Buttgens N, Nath R, Mahajan A V and Loidl A 2007 Phys. Rev. B 76 064429
[19] Takeya T, Ishida K, Kitagawa K, Hara Y, Onuma K, Maeno Y, Nambu Y, Nakatsuji S, MacLaughlin D E, Koda A and Kadono R 2008 Phys. Rev. B 77 054429
[20] Motome Y, Nakamikawa K, Yamaji Y and Udagawa M 2010 Phys. Rev. Lett. 105 036403