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NMR Studies of the Antiferromagnetic Heavy Fermion Compound CePdAl

Akira OYAMADA, Kazuo KAMIOKA, Kenjiro HASHI, Satoru MAEGAWA, Takao GOTO and Hideaki KITAZAWA[1]

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-01
[1]*National Research Institute for Metals, Tsukuba 305*

Magnetic properties of CePdAl have been investigated by ^{27}Al NMR and magnetic susceptibility measurements. A large anisotropy of susceptibility suggests that CePdAl is an Ising-like system. The antiferromagnetic transition at 2.7 K has been observed by magnetic susceptibility measurements and NMR spin-echo spectra and spin-lattice relaxation rate T_1^{-1}. In contrast with a similar heavy fermion compound $CePd_2Al_3$, T_1^{-1} shows the development of short range magnetic correlations far above the antiferromagnetic transition temperature. The incommensurate magnetic structure was observed by the spin-echo spectra. To explain the difference between CePdAl and $CePd_2Al_3$, a possibility of two-dimensional character in CePdAl is discussed.

KEYWORDS: CePdAl, Antiferromagnet, Heavy Fermion, Kagomé lattice, susceptibility, NMR

§ 1. Introduction

Recently, an antiferromagnetic heavy fermion compound $CePd_2Al_3$ has been investigated extensively to compare with the new heavy fermion superconducting compounds UPd_2Al_3 and UNi_2Al_3 [1)-6)]. These three compounds have the same crystal structure (hexagonal $PrNi_2Al_3$-type). However, $CePd_2Al_3$ does not show superconductivity. The electronic specific heat coefficient(γ) of $CePd_2Al_3$ was estimated to be 380 mJ / mol K^2 [1)]. This large γ is typical property of heavy fermion compounds. The most important point is that the $CePd_2Al_3$ is close to the magnetic and nonmagnetic boundary. This situation can cause a large sample dependence.

Because of the large anisotropy, a separate treatment of the two interactions, the f-d hybridization($J_{d\text{-}f}$) in the c-plane and the RKKY-type exchange interactions(J_z) between the planes were proposed as follows [3)]. The f-d hybridization in the c-plane is rather strong because in c-plane Pd atoms are very close to Ce atoms. While J_z which is mediated by isolated Al atoms is rather small. The reduced Ce 4f moments are magnetically correlated in c-plane and Jz between correlated planes leads the system to three-dimensional long-range magnetic order. This model could explain both the sample dependence and the pressure dependence of Néel temperature [7)].

CePdAl was reported as a new antiferromagnetically ordered heavy fermion compound [8)9)]. The temperature dependence of its resistivity shows the typical Kondo effect.

The crystal structure of CePdAl is a hexagonal ZrNiAl type. The space group is P62m with sites(3f) occupied by Ce, (1a) and (2d) by Pd and (3g) by Al [10)]. The magnetic properties of CePdAl are quite similar to those of $CePd_2Al_3$ though the crystal structure is different. Both CePdAl(111) and $CePd_2Al_3$(123) exhibit antiferromagnetic orderings at almost the same temperature, 2.7K and 2.8K respectively. γ value of (111) is estimated to be 270 mJ / mol K^2 which is a little smaller than that of (123) [10)]. This smaller γ suggests that Kondo temperature (T_K) is larger [8)]. The entropy at the magnetic transition temperature (T_N) is 0.38Rln2 ,which is the similar value to 0.4Rln2 of (123). Recently, specific heat measurement of CePdAl in high pressure was reported [11)]. This measurement shows that CePdAl is close to the magnetic and nonmagnetic boundary as well as (123).

However, some different behaviors between (111) and (123) have been reported. The specific heat anomaly at T_N has a large tail at higher temperature side in (111) ,which suggests strong short range correlations from rather high temperatures. Neutron scattering measurements show that the magnetic structure of (111) is quite different from that of (123). Each propagation vector of (111) and (123) is k=[1/2,0,0.35] and k=[0,0,1/2] ,respectively [12)].

To clarify the strong short range correlations and the magnetic structure of CePdAl, magnetic susceptibility measurements and NMR measurements were performed.

§ 2. Experimental Procedures

Polycrystalline samples of CePdAl were prepared by arc melting method with starting materials of 3N-Ce, 3N-Y, 3N-Pd and 5N-Al in an argon atmosphere. The details of the sample preparation were reported in reference [1)]. X-ray diffraction confirmed that the obtained polycrystals are single phases of the hexagonal ZrNiAl type structure. The lattice parameters at room temperature are a=7.2210 and c=4.2334 ,respectively.

Magnetic susceptibility measurements were performed by SQUID spectrometer between 2K and 300K under a magnetic field of 1kOe.

^{27}Al NMR measurements were performed by the phase-coherent type spectrometer. The powder samples are prepared by crushing polycrystals to avoid the skin effect. The NMR spectra were obtained by observing the spin-echo intensity sweeping magnetic field at a constant frequency. Spin-lattice relaxation rate T_1^{-1} was measured by observing the recovery of the spin-echo intensity after a comb sequence of rf pulses. Spin-spin relaxation rate T_2^{-1} was measured by observing the spin-echo intensity with increasing interval time between first pulse and second pulse.

§ 3. Experimental Results

Figure 1 shows the temperature dependence of an NMR spin-echo spectrum at 4.2K using free powder of CePdAl. This spectrum consists of five peaks which are clearly separated from each other. The characteristic feature is that the five peaks are equally separated. The separation is 0.489 kOe. This is the typical spin-echo spectra due to the first order effect of the electric quadrupolar interaction. Furthermore each intensity of (5/2 ↔ 3/2), (3/2 ↔ 1/2), (1/2 ↔ -1/2), (-1/2 ↔ -3/2) and (-3/2 ↔ -5/2) transitions is quite consistent with the expected ratio from $|\langle m|I_x|m-1\rangle|^2$,5:8:9:8:5. Therefore it seems that there is no effect of the second order of the electric quadrupolar interaction and asymmetry parameter (η) in this spectrum. However, in terms of low symmetry of Al sites, η is expected not to be zero. Then the spectrum in figure 1 is expected ,when c-axis is easy axis and the powder is well-oriented parallel to easy axis. To confirm this speculation, the powders were oriented parallel to easy axis in a magnetic field of 8T at room temperature and were fixed by Polyethylene Glycol. Using these powders, NMR measurements were performed with the magnetic field applied in vertical direction parallel to the easy axis. The obtained spectrum at 4.2K is shown in figure 2. This spectrum clearly shows the typical two-dimensional powder pattern with $\eta \neq 0$. Therefore we conclude that the easy axis of CePdAl is c-axis and the powder can be well-oriented parallel to c-axis. This situation allows us to perform each magnetic measurement along c-axis and in c-plane using the fixed powder. From now on, we only index each measurement to c-axis and c-plane. Finally, the electric quadrupole frequency (ν_Q) and η are estimated to be 0.542MHz and 0.27, respectively.

Figure 3(a) shows the temperature dependence of magnetic susceptibility of CePdAl. Magnetic susceptibility shows a large

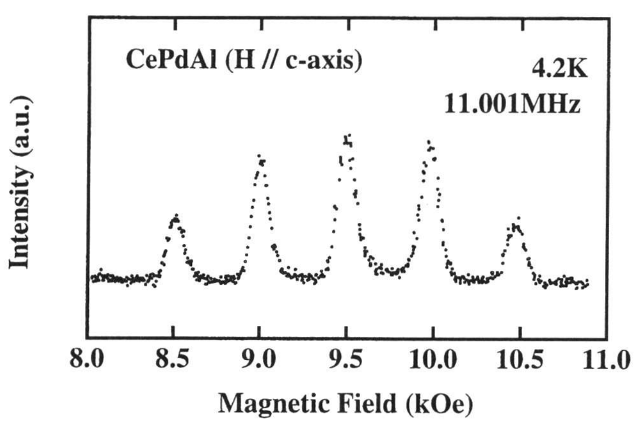

Fig.1 ^{27}Al Spin-echo spectra of powder samples of CePdAl at 4.2K using NMR frequency of 11.001MHz. The powders are well-oriented along c-axis.

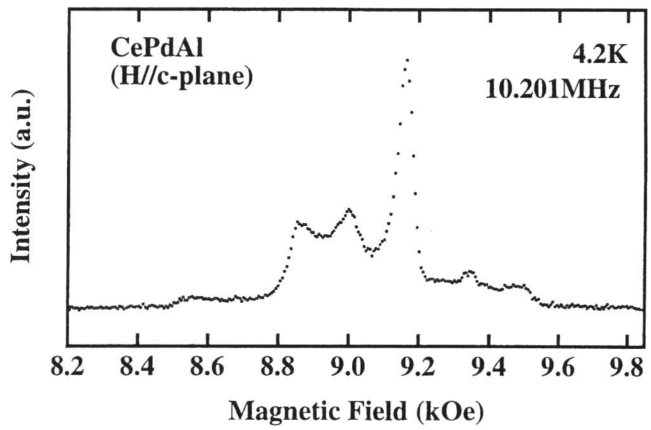

Fig.2 ^{27}Al Spin-echo spectra of fixed powder samples of CePdAl at 4.2K using NMR frequency of 10.201MHz. Magnetic field is applied in the direction of c-plane.

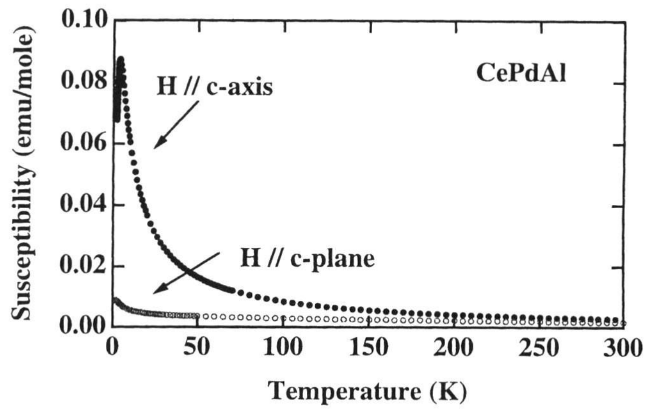

Fig.3(a) Temperature dependence of magnetic susceptibilities in both directions, c-axis and c-plane. Applied magnetic field is 1kOe.

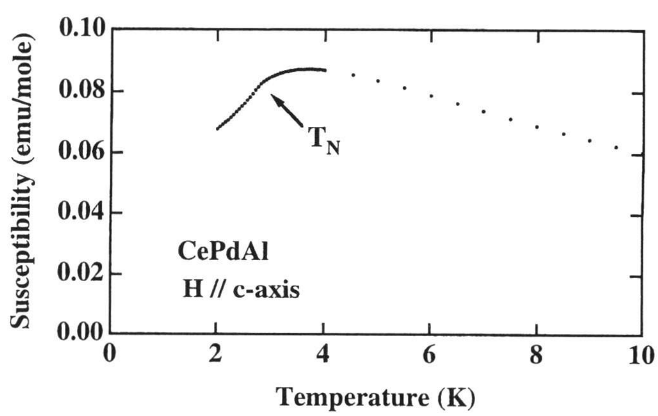

Fig.3(b) Lower temperature part of the temperature dependence of the magnetic susceptibility along c-axis.

anisotropy. This shows CePdAl is an Ising-like system. Figure 3(b) shows the low temperature part of fig.3(a). The susceptibility shows a broad maximun around 4K and a small anomaly of the slope at 2.7K. To observe the small anomaly at 2.7K more clearly, the derivative of the susceptibility ($d\chi/dT$) in both directions is calculated (figure 4). The temperature dependence of $d\chi/dT$ shows a clear maximum at 2.7K in both direction ,which suggests that antiferromagnetic order ocurrs at

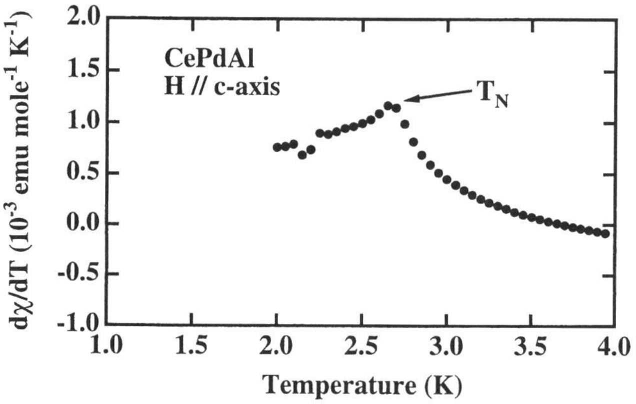

Fig.4 Temperature dependence of the temperature derivative of the magnetic susceptibility in the direction of c-axis.

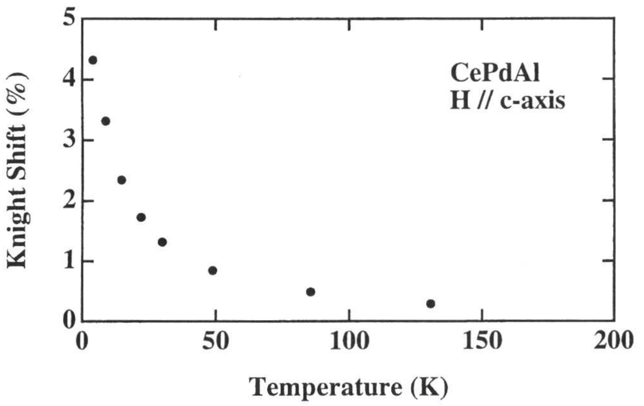

Fig.5 Temperature dependence of Knight shift along c-axis.

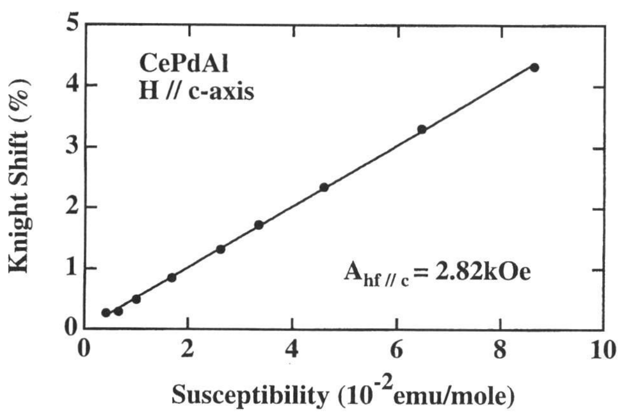

Fig.6 Knight shift vs susceptibility plot of CePdAl along c-axis. The plot shows a linear relation in whole temperature range.

2.7K. This ordering temperature is quite consistent with previous specific heat measurements [8]. It is noticeable that the temperature of the broad maximum is 3.7K while the Néel temperature is 2.7K. Then there is about 30% of deviation between the broad maximum and Néel temperature. This deviation reminds us of the two-dimensional Ising lattices [13]. Anyway a broad maximum of susceptibility suggests strong short range correlations above Néel temperature.

Figure 5 shows the temperature dependence of Knight shift (K) along c-axis. Knight shift shows the similar temperature

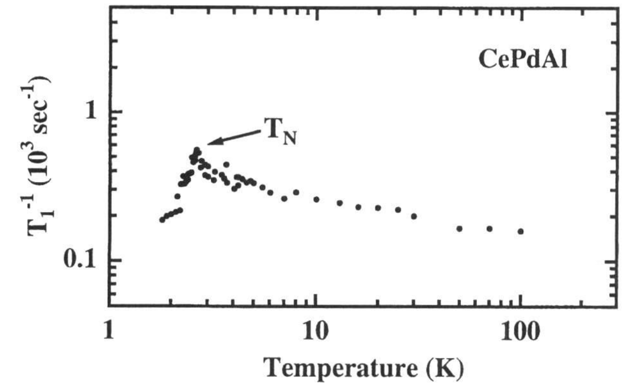

Fig.7 Temperature dependence of spin-lattice relaxation rate T_1^{-1} measured at the central peak of (1/2 ↔ -1/2) transition. Used NMR frequency is 14.96MHz.

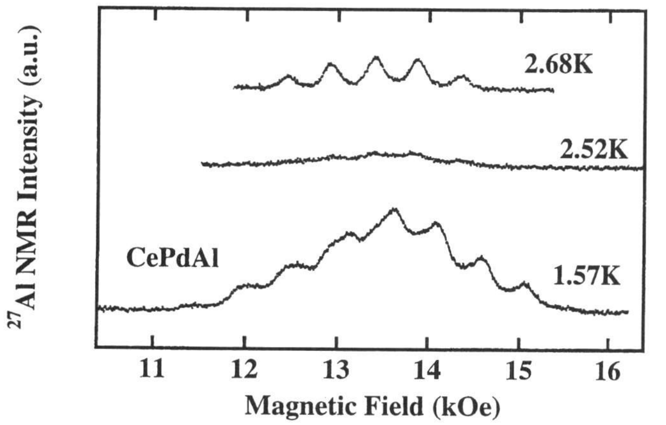

Fig.8 ^{27}Al Spin-echo spectra of powder samples of CePdAl at various temperatures, 4.2K, 2.5K and 1.5K at a frequency of 14.96MHz.

dependence as magnetic susceptibility (χ). Figure 6 shows K vs χ plot. K vs χ plot is almost linear in whole temperature range. The transferred hyperfine coupling (A_{hf}) is estimated to be 2.82 kOe/μ_B.

Figure 7 shows the temperature dependence of spin-lattice relaxation rate T_1^{-1}. There is a sharp peak at T_N ,which is consistent with susceptibility measurements. Above T_N, T_1^{-1} decreases with increasing temperature. This suggests the strong short range correlations ,which is consistent with susceptibility measurements and previous specific heat measurements again. Below T_N, T_1^{-1} rapidly decreases with decreasing temperature. It seems that spin wave excitation dominates the temperature dependence of T_1^{-1} below T_N. Korringa relation expected from the large γ value of specific heat is not very clear in experimental temperature range so far.

To investigate the magnetic structure in detail, spin-echo spectra were observed at various temperatures (figure 8). Above T_N, spin-echo spectra consist of five peaks which are equally separated. Below T_N, the overall feature of spin-echo spectra is almost the same but the width of each peak becomes a little larger. The most characteristic feature is that the intensity of spin-echo spectra gradually decreases below T_N. It seems that the minimum of the intensity occurs around 2.5K ,which is not the same temperature as T_N. Below 2.5K, the intensity increases gradually with decreasing temperature and

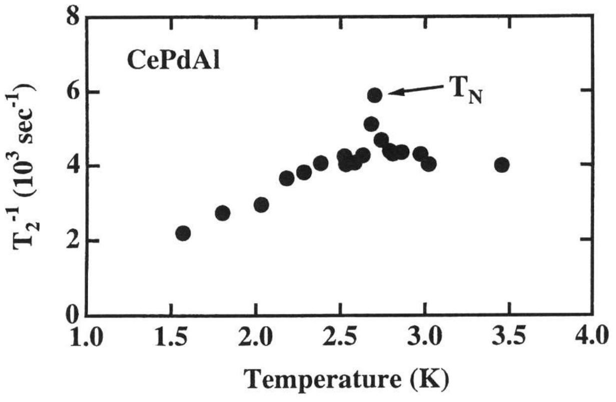

Fig.9 Temperature dependence of spin-spin relaxation rate T_2^{-1} at a frequency of 14.96MHz.

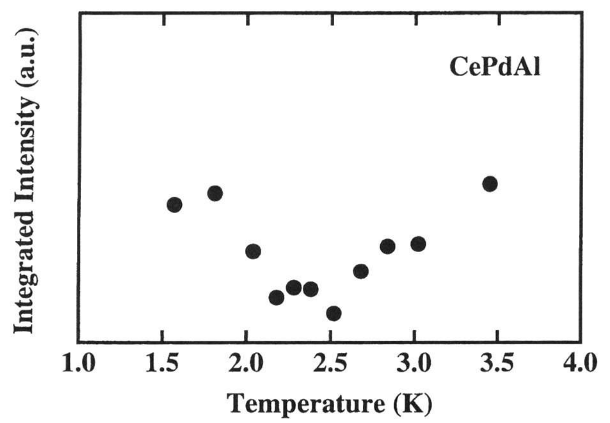

Fig.10 Temperature dependence of the integrated intensities of spin-echo spectra. T_2 and temperature effects are calibrated.

the spectra consist of seven peaks. This situation suggests that the magnetic ordering is not very simple in CePdAl. To investigate the temperature dependence of the intensity of spin-echo spectra in detail, spin-spin relaxation rate T_2^{-1} was measured around ordering temperature. Figure 9 shows the temperature dependence of T_2^{-1}. There is a sharp peak at T_N again. Then the integrated intensity of the spin-echo spectra at each temperature is estimated. Furthermore temperature and spin-spin relaxation rate effect are calibrated when the integrated intensities are estimated. Figure 10 shows the temperature dependence of the integrated intensity of spin-echo spectra. Below T_N, the intensity starts to decrease with decreasing temperature and reaches the minimum value at 2.5K. Below 2.5K, the intensity gradually recovers with decreasing temperature. It suggests that there is an another anomaly around 2.5K except T_N.

§ 4. Discussions

4-1 Short Range Correlations

Magnetic susceptibility and spin-lattice relaxation rate measurements suggest that there are rather strong short range correlations above T_N in CePdAl. These are consistent with previous specific heat measurements [10]. The physical properties of CePdAl are reported to be similar to $CePd_2Al_3$ [8]. However, our measurements show that the development of short range correlations in (111) is different from that of (123). The difference of crystal structure of these two compounds may give us a hint to understand the physical properties.

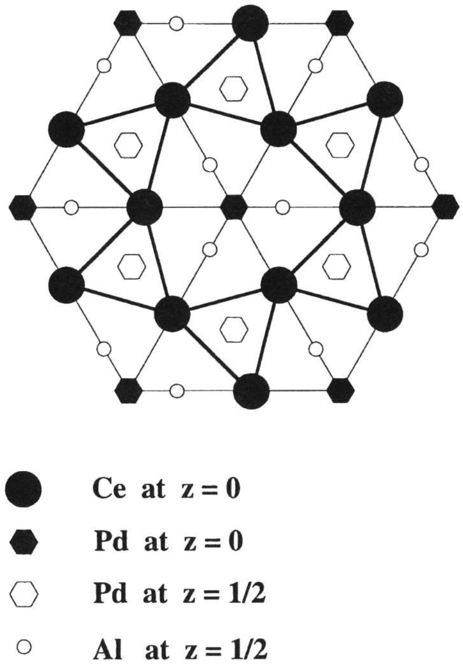

Fig.11 Projection onto c-plane of the crystal structure of CePdAl.

Figure 11 shows the crystal structure of CePdAl projected to c-plane. The typical feature is the layer structure of Ce atoms in c-plane ,which is quite different from that of (123). The distance between the nearest neighbor Ce atoms in the direction of c-axis and c-plane is 4.233Å and 3.722Å ,respectively. While that of (123) is 4.216Å and 5.471Å ,respectively. The distance between the nearest neighbor Ce atoms in c-plane of (111) is quite small relatively. Therefore the strong magnetically correlated two-dimensional plane is expected in CePdAl. Now we speculate that small distance between Ce atoms can cause the strong c-f mixing and make the strong exchange interactions between Ce atoms and lead to Kondo effect. This causes the two-dimensional magnetic behavior as observed in magnetic susceptibility and T_1^{-1}. The interesting point is that Ce atoms in c-plane form Kagomé lattice which is a variation of triangular lattice. The characteristic feature of Kagomé lattice is that the number of the nearest neighbor atoms at each magnetic sites are 4 while those of triangular lattice are 6. This loose circumstance from neighbors causes the large degeneracy and peculiar physical properties [14)15)]. The investigation about dynamical properties in this line seems quite interesting although the theoretical approach is not enough for the moment. From these discussions, CePdAl is the first Ce compound which shows heavy fermion properties on Kagomé lattice.

4-2 Magnetic Structure

The different nature of magnetic orderings in (111) from that of (123) can be expected from strong two-dimensional short range correlations as mentioned before. Actually neutron diffraction measurements have observed k-vector of magnetic ordering in CePdAl at lowest temperature. The obtained k-vector is [1/2,0,0.35] while that of (123) is [0,0,1/2]. At first we discuss about magnetic structure at lowest temperature. As seen in figure 8, spin-echo spectra consist of clearly resolved seven peaks. This suggests that the magnetic structure should be a commensurate one. This is discrepant with the k-vector obtained by neutron diffraction measurements. This is an open question for the moment. However, we should note that k-vector [1/2,0,0.35] is very close to the commensurate one [1/2,0,1/3]. As mentioned before, Ce atoms form Kagomé lattice in c-plane. This strong frustration possibly affects the magnetic structure. More detailed experiments are required to clarify the magnetic structure at lowest temperature.

Below T_N, the decrease of integrated intensity of spin-echo spectra was observed down to 2.5K. The most probable explanation is that there is an incommensurate magnetic structure below T_N. In incommensurate magnetic phase, the internal magnetic field at Al sites has various magnitude. That causes spread out of spin-echo spectra. This situation is quite consistent with the decrease of integrated intensity below T_N. Furthermore the gradual recovery of intensities below 2.5K was observed. This shows that the sharp transition like lock-in transition is not the case. It seems that incommensurate k-vector gradually changes into commensurate one with decreasing temperature.

In the case of UPd_2Al_3, the incommensurate magnetic orderings were observed by neutron diffraction measurements [16)17)]. However, the other measurements did not observe these incommensurate structures [18)]. The sample dependence may be the reason of this discrepancy, if the observation of these incommensurate structures is not ascribed to experimental errors. It should be noted that these incommensurate structures including that of CePdAl are all modulated structures in the direction of c-axis.

In reference 3), it was proposed that three-dimensional long-range magnetic order in $CePd_2Al_3$ was generated by the exchange interactions between magnetically correlated planes. Furthermore the strong sample dependence of T_N can be explained by deficiency or displacement of Al atoms ,which mediate the RKKY-type interactions between the planes. Then we speculate that the modulation in the direction of c-axis is possibly driven by the exchange interactions between planes. The deficiency or displacement of Al atoms may generate the large sample dependence of these incommensurate structures.

Among these compounds, two-dimensional magnetic correlations in CePdAl seem to be the strongest because of the nearest distance between Ce atoms in c-plane. This strongly correlated Ce planes order magnetically due to the exchange interactions between planes similar to (123) case. However, the sample dependence of CePdAl may not be so large. Because the exchange interactions between planes are mediated by not only isolated Al atoms but also Pd atoms in contrast to (123) cases. The investigation of the single crystal and the sample dependence of CePdAl is required to confirm the complicated magnetic orderings.

§ 5. Conclusions

Magnetic properties of the antiferromagnetic heavy fermion compound CePdAl were investigated by magnetic susceptibility and NMR measurements. Both results show the strong short range correlations which are consistent with previous specific heat measurements. The two-dimensional magnetic correlations on Kagomé lattice are discussed. The Néel temperature (2.7K) obtained by all measurements, magnetic susceptibility, T_1^{-1}, T_2^{-1} and previous specific heat are quite consistent. The incommensurate magnetic structure was observed by the integrated intensity of spin-echo spectra. The importance of the exchange interactions between magnetic correlated planes is discussed to understand the complicated magnetic structures.

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