Neutron Powder Diffraction Study of the Magnetic Structure of $NdPd_5Al_2$

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Magnetic structure of $NdPd_5Al_2$ has been studied by means of neutron powder diffraction. We observed the magnetic reflections with the modulation vector q= (1/2 0 0) below the ordering temperature T_N.We found a collinear magnetic structure of Nd moment of 2.7(3) μ_B at 0.5 K parallel to the c-axis, where the ferromagnetically ordered a-planes stack with four Nd layer period of $++--$ sequence along the a direction with the distance between adjacent Nd layers to be $a/2$ (magnetic space group P_anma). This 'stripe'-like modulation is very similar to $CePd_5Al_2$ with q=(0.235 0.235 0) and the Ce moment parallel to the c-axis. These structures with in-plane modulation are consequence of the two dimensional nature of fermi surface topology in this family, coming from unique crystal structure with very long tetragonal unit cell and large distance > 7 Å between the rare earth layers separated by Al and two Pd layers.

KEYWORDS: $NdPd_5Al_2$, $NpPd_5Al_2$, magnetic structure, neutron diffraction

1. Introduction

The heavy fermion superconductivity in $NpPd_5Al_2$[1)] attracts strong interests in the field of strongly correlated electron systems. This compound is known as the first example of the Np-based superconductor. The heavy fermion nature (electronic specific heat constant γ =200 mJ/(K^2·mol)) has been observed at low temperatures with non-fermi liquid behavior in the temperature dependence of the resistivity. It becomes superconducting below the relatively high transition temperature T_c= 4.9 K. The xy-type anisotropy in the magnetic susceptibility with the easy plane perpendicular to the tetragonal c-axis suggests the two dimensional nature in the electronic structure. Remarkable cylindrical fermi surfaces as well as pancake- or doughnut-like shape were revealed by a band calculation, where the fermi level is located at the narrow f band with large density-of-state.[2)] This two-dimensionality is attributed to the unique crystal structure with a very long body-centered tetragonal unit cell ($I4/mmm$) and very large Np interlayer distance $c/2 > 7$ Å separated by two Pd and one Al layers, while a ~4.1 Å is also very large. Therefore it is expected that $5f$ electrons remain localized character. A recent Mössbauer study empirically concluded the Np valence close to the trivalent state Np^{3+} from the isomer shift. This is consistent with the band calculation which predicts the number of $4f$ to be 3.7, roughly corresponding $Np^{3.3+}$, which is slightly deviates from the trivalent state. The NMR study reported the d-wave superconductivity mediated by xy-type magnetic fluctuation.[3,4)]

The mechanism of unusual heavy fermion nature and the superconductivity as well as the $5f$ electronic state is of particular interest, but the strict regulation for nuclear materials makes difficult for further investigations. For example, the dynamical magnetic correlation remains open question. In this situation, iso-structural rare earth family RPd_5Al_2 is helpful to shed light on the unusual behavior of the Np compound; RPd_5Al_2 (R:Y, Ce, Pr, Nd, Sm, Gd) has been systematically synthesized.[6)] Antiferromagnetic transitions were reported in this series (except for Y and Pr compound with singlet ground state), where de Gennes scaling of T_N were more or less confirmed except for $CePd_5Al_2$. RPd_5Al_2 (R: Tb-Yb) series as well as the new RPt_5Al_2(R:Y, Gd-Tm, Lu) has been prepared very recently.[7)] The magnetic structure[8)] and a complicated magnetic phase diagram n $CePd_5Al_2$ have been revealed.[9,10)] An incommensurate sinusoidal modulation with q= (0.235 0.235 0) was reported below T_{N1}= 4.1 K, while square up of the modulation was suggested from the observation of the third order harmonics below T_{N2}= 2,9 K. The Ce moment as large as 2 μ_B is parallel to the c-axis. Surprisingly, a pressure induced superconductivity has been reported in $CePd_5Al_2$.[9,10)]

Neutron scattering study of $NdPd_5Al_2$ is highly interesting

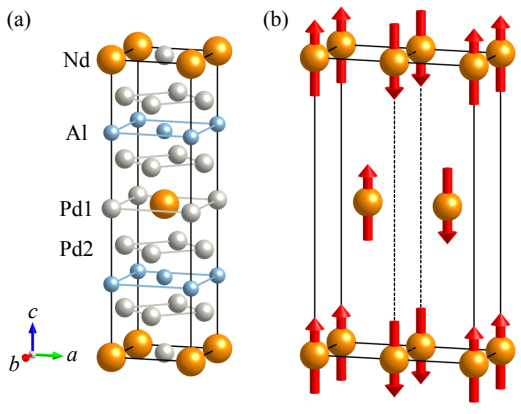

Fig. 1. (Color online) (a) The crystal structure of $NdPd_5Al_2$. (b) The magnetic structure with q= (1/2 0 0) and Nd moment as large as 2.7(3) μ_B revealed in this study.

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to clarify the magnetic correlation in this family. The crystal structure of $NdPd_5Al_2$ is shown in Fig. 1(a). This compound shows antiferromagnetic ordering below the ordering temperature T_N= 1.2 K[6] or 1.3(1) K.[11] Fig. 1(b) shows the magnetic structure of $NdPd_5Al_2$ revealed in this study. We present the experimental procedures, results, and discussions below.

2. Experimental Procedure

Polycrystalline samples of $NdPd_5Al_2$ were grown by arc melting of stoichiometric amount of Nd (3N), Pd (3N5), and Al (5N) in a pure Ar atmosphere. Totally 20 g of as-grown samples were mechanically cut in small pieces and sealed in an aluminum can filled with ^{4}He thermal exchange gas. The sample was checked by x-ray powder diffraction. No impurity was detected.

Unpolarized neutron diffraction data were collected on the wide-angle neutron diffractometer WAND (HB-2C) installed at the High Flux Isotope Reactor (HFIR) in the Oak Ridge National Laboratory (ORNL), USA. An incident neutron beam with a wavelength of 1.4827 Å was obtained from a Ge(1 1 3) monochromator. The sample was cooled down to 0.3 K with a ^{3}He cryostat. The diffraction pattern at paramagnetic state (3.0 K) was analyzed by the Rietveld refinement method with the software Fullprof.[12] The magnetic scattering in the ordered state was also calculated using the same software. The crystal and magnetic structures were drawn with the software VESTA.[13]

3. Results

Figure 2 shows the temperature dependence of the diffraction data of $NdPd_5Al_2$ in the paramagnetic phase at 3.0 K down to 0.3 K in the antiferromagnetically ordered phase. We clearly observed antiferromagnetic reflections below T=1.22 K. The antiferromagnetic reflections disappear above T=1.37 K. The ordering temperature T_N is expected between these temperatures, which is consistent with previous studies.[6,11] On the other hand, no remarkable shift or separation of nuclear peaks were detected. It means the absence of significant change in the crystal structure within the sensitivity and the resolution of the WAND instrument. We confirmed that the nuclear scattering profile of the paramagnetic phase can be explained with the same crystal structure as in RPd_5Al_2 (space group $I4/mmm$), where the crystal parameters at 3.0 K were determined as a = 4.120(1) Å, c = 14.823(2) Å, and the atomic positions Nd(2a) (0, 0, 0), Pd1(2b) (0, 0, 1/2), Pd2(8g) (0, 1/2, 0.146(1)), Al(4e) (0, 0, 0.257(2)) with the reliability factors R_{wp} = 12.0, R_e = 4.93, R_B = 7.34, and $\chi^2 = (R_{wp}/R_e)^2$ = 5.93, respectively. All the isotropic atomic displacement parameters B_{iso} were fixed at 0.1 Å^2 during this refinement. These are consistent with a recent result of x-ray powder diffraction measured at room temperature.[11]

We observed clear antiferromagnetic reflections, where the peak positions were well explained by the modulation vector of q=(1/2 0 0) as shown in Fig. 3. The magnetic contribution was obtained by subtracting the paramagnetic nuclear contribution (T=3.0 K) from the data at T= 0.5 K. The peak positions of the observed magnetic reflections are in perfect agreement with those for q=(1/2 0 0) as denoted by short bars. We can clearly recognize that the magnetic intensity decreases significantly with increasing the Miller index l. For example, the (1/2 0 l) reflections with l=0~3 show a significant decrease with increasing of l, despite the multiplicity. No peak is recognizable for l > 4 beyond the statistical error of the background. This result can be understood with so called angle factor in the magnetic structure factor calculation. The magnetic component in the plane perpendicular to the scattering vector Q of neutron contributes to the magnetic scattering. Therefore the steep decrease of the magnetic scattering with Q approaching to the c direction involves the fact that the Nd magnetic moments are parallel to the c-axis. This is consistent with the Ising anisotropy of the magnetic susceptibility in $NdPd_5Al_2$ with the easy axis parallel to the c-axis.[11] The solid line in Fig. 3 shows the calculated intensities of magnetic reflections, assuming a simple collinear magnetic structure of Nd moment parallel to the c-axis, consisting of up(+) up(+) down(−) down(−), namely + + − − sequence along the a-axis (magnetic space group P_anma), which is schematically shown in the inset of Fig. 3. The magnetic structure factor ($d\sigma/d\Omega$) is given as

$$\left(\frac{d\sigma}{d\Omega}\right) = 8A^2\left|M\right|^2 \sin^2\phi \qquad (1)$$

Here A= 2.7×10^{-15}m is the electronic magnetic-scattering length, ϕ is the angle between the scattering vector Q and Nd moment $M = g_J f(Q) J$. $f(Q)$ is the magnetic form factor. The Nd ordered moment of about 2.7(3) μ_B at 0.5 K was estimated from the structure factor calculation with R_{mag} <11%, typically. This large value in Nd compounds is consistent with gJ= 3.2 μ_B of Nd^{3+} free ion. A somehow smaller value of the experimentally observed magnetic moment may be understood via a crystalline electric field (CEF) effect.

Strictly speaking, the magnetic structure with + 0 − 0 stacking sequence along the a-axis, namely Nd atoms on the corner site having magnetic moment, but no moment at body centered positions (magnetic space group, P_amma) provides the same diffraction profile as calculated using eq. (1). The scattering cross section in this case also depends only on the angle factor, given as $4A^2|M|^2 \sin^2\phi$. The difference of the factor is due to the absence of Nd moment at the body centered site. From the consequence of this difference of the factor, the Nd

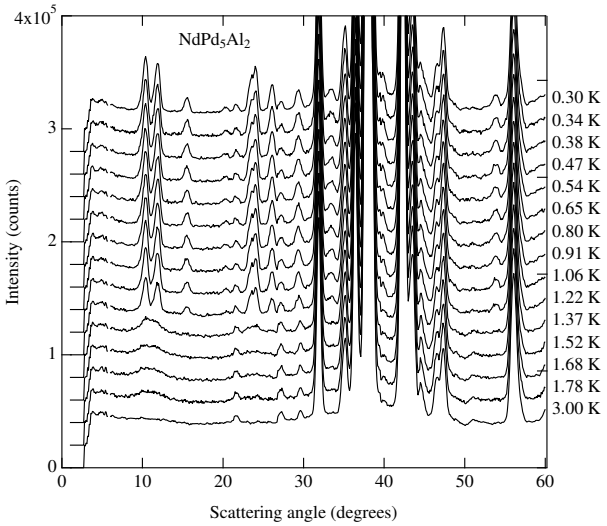

Fig. 2. The temperature dependence of the neutron powder diffraction data of $NdPd_5Al_2$.

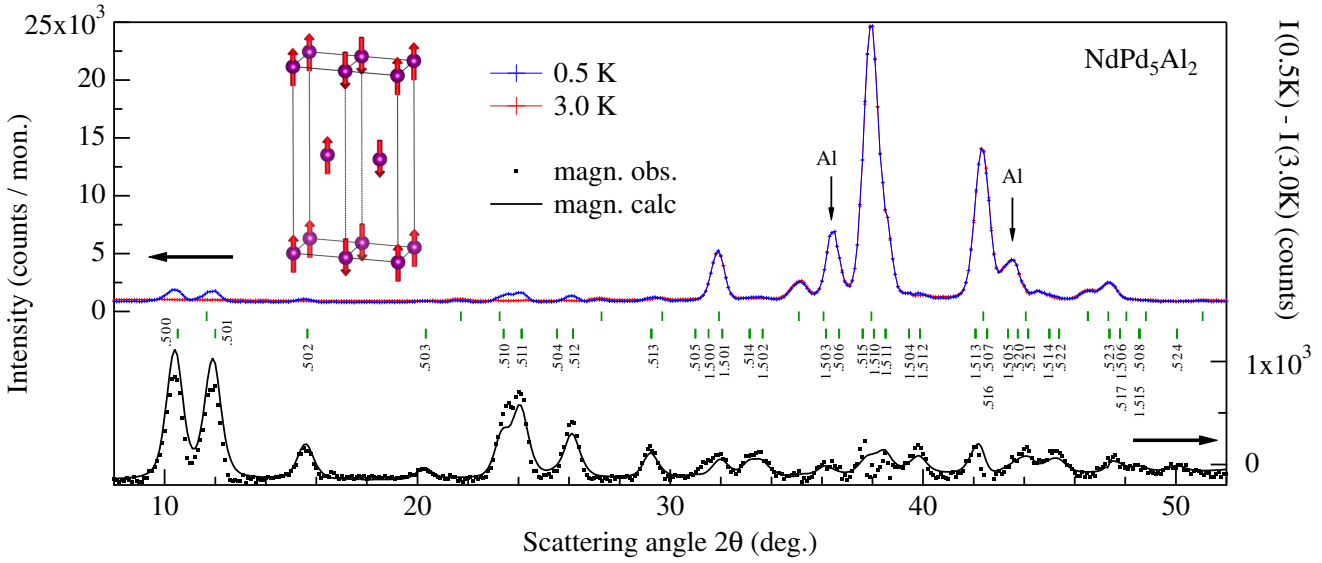

Fig. 3. (Color online) The powder diffraction data of $NdPd_5Al_2$ measured at 3.0 K and 0.5 K. The dots and solid line indicate the magnetic contribution obtained by the difference I(0.5 K) - I(3.0 K) and the calculated magnetic diffraction pattern, respectively. The short bars indicate the peak position of the nuclear (upper) and antiferromagnetic (lower) reflections. The inset shows the experimentally determined magnetic structure of $NdPd_5Al_2$.

moment of this structure is obtained as 3.9 μ_B by multiplying $\sqrt{2}$ by that of our estimation 2.7 μ_B using eq. (1). The ordered moment larger than even the effective moment 3.58 μ_B of free ion Nd^{3+} is unrealistic. Furthermore the observed magnetic entropy $R \ln 2$ released by the antiferromagnetic transition[11] should be the half of the observed value, when the half of the Nd atoms remain paramagnetic below the transition temperature. Assuming pseudo-quartet state to avoid inconsistency of magnetic entropy again disagrees with the moment size.

Since the tetragonal symmetry was broken by the antiferromagnetic ordering, the a- and b-axis is not equivalent in the magnetically ordered phase. However, the difference in the in-plane lattice constant can be undetectably small within rather low angle resolution of WAND instrument. The collinear structures with q=(1/2 0 0), namely + + − − or + 0 − 0 sequence and the magnetic moments either parallel to a or b axis are allowed from the group theoretical point of view. Obviously these four structures are ruled out from the present neutron diffraction data. No multi-q structure is allowed for this case of Ising type (M//c) and the in-plane modulation q=(1/2 0 0), which could maintain the in-plane tetragonal symmetry.

Figure 4 shows the temperature dependence of the (1/2 0 l) antiferromagnetic peak intensity for l=0~3. We observed remarkable increases of the intensities with decreasing temperature. A small enhancement of the magnetic scattering intensity below 0.5 K can be interpreted as the hyperfine enhancement of ^{143}Nd and/or ^{145}Nd nuclei (both I=7/2) with natural abundance of 12.2 and 8.5 %, respectively. The cross section of the hyperfine term is proportional to the incoherent scattering length and the average of the nuclear spin operator. In the Nd-case both nuclei have strong incoherent scattering, especially ^{143}Nd is comparable to proton. The procedure for detail analysis of this effect have been published in previous studies of *e.g.* $HoBa_2Cu_3O_7$[14] or $NdFeO_3$.[15] In fact, the hyperfine enhancement has been observed for many Nd-compounds.[16] For unpolarized neutron, the contribution from the hyperfine enhancement provides an additional terms to the cross section for the magnetic structure factor in eq. (1); this contribution is independent of the scattering vector Q. As said above, it is proportional to the average of the nuclear spin operator. While 0.5 K is too high to allow a fully polarized state, the temperature is low enough to give the average a non-zero value.

Nowadays the hyperfine structure of rare earth nuclei can be measured by high resolution neutron back scattering spectrometer.[16,17] It has been reported that the hyperfine splitting of Nd nuclei can be scaled by the size of the Nd magnetic moment, which provides the internal field at nuclear site.[16] From the present result of 2.7 μ_B, the splitting between two levels with $\Delta I \pm 1$ is expected to be ~3.5 μeV. The total splitting between I=±7/2 can be obtained as ~3.5×7=~25 μeV,

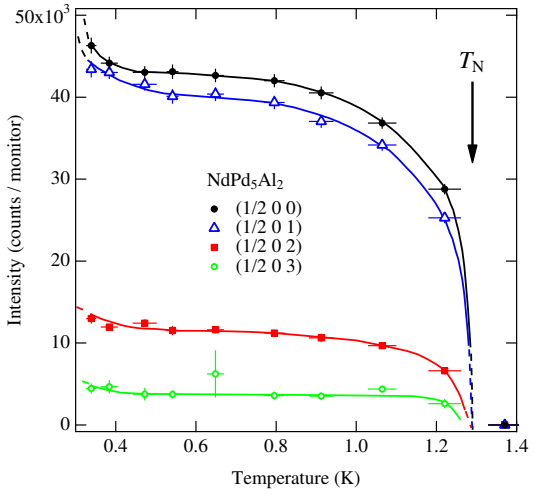

Fig. 4. (Color online) The temperature dependence of the peak intensities of the (1/2 0 l) antiferromagnetic reflections for l=0~3 observed in $NdPd_5Al_2$. The intensities were obtained by Gaussian fitting. The lines are guides for eyes.

which roughly corresponds to ~0.2 K, comparable to the lowest temperature in this study. Therefore, the finite polarization of the nuclear magnetic moment can be realized even in the temperature range attainable by a ^{3}He cryostat, which is rather high for the observation of the nuclear magnetic order. One possible reason is that the hyperfine field at the Nd-site is very strong in $NdPd_5Al_2$ as suggested by the large value of the Nd-moments. It would be interesting to measure the incoherent inelastic contribution in this compound to evaluate the hyperfine field at the nucleus.

As shown in Fig. 4 the nuclear contrubution was clear but negligibly small down to 0.3 K. Furthermore, the analysis with additional parameters to take the nuclear magnetic contribution into account may not be reliable using the present data with relatively strong background. Therefore we estimated the moment size from the data measured at 0.5 K, and ignored the nuclear contribution.

4. Discussion

The obtained magnetic structure shown in the inset of Fig. 3 is highly interesting in comparison with $CePd_5Al_2$.[8] The projection of the magnetic structures on to the c-plane are shown in Fig. 5. The magnetic structure in $NdPd_5Al_2$ consists of + + − − modulation including four Nd layers in a period as shown in Fig. 5(a). If we assume the incommensurate propagation q=(0.235 0.235 0) in $CePd_5Al_2$ to be approximately the commensurate one with q=(1/4 1/4 0), then the magnetic structure is also described by the + + − − sequence with four Ce layers period but along the [110] direction, as in Fig. 5(b). These 'stripe'-like structures break the tetragonal symmetry, and cannot be understood in terms of super-exchange interactions and the paramagnetic crystal symmetry. Instead, they should be interpreted in terms of RKKY interaction. It is of remarkable importance that both compounds show only in-plane modulation $q_{\|}$, the amplitudes $|q_{\|}| = 0.33|a^*|$ for $CePd_5Al_2$ and $0.5|a^*|$ for $NdPd_5Al_2$, are small and comparable. The cylindrical electron and hole fermi surfaces have been reported in the band calculation of $4f$-itinerant $CePd_5Al_2$ and non-$4f$ reference compound $LaPd_5Al_2$.[10] The experimentally observed fermi surfaces in $CePd_5Al_2$, and also $PrPd_5Al_2$, have been reported to be similar with those for $LaPd_5Al_2$,[10] which reflects fermi surface topology of RPd_5Al_2 with localized $4f$ electrons. Namely $4f$ electrons in $CePd_5Al_2$ and also $PrPd_5Al_2$ are well localized. The dominant RKKY interaction mediated by the conduction electrons with cylindrical fermi surfaces can be expected to be described with the modulation only with in-plane component $q_{\|}$ as observed in $CePd_5Al_2$ and $NdPd_5Al_2$ in a previous and the present study, respectively. The exact size and in-plane direction of the propagation vector may depend on the size of the fermi surface as well as the interaction Hamiltonian including $4f$ and conduction electron orbitals, thus the detail of the electronic structure.

According to the mean field calculations for $CePd_5Al_2$ and $PrPd_5Al_2$, the Ising-type magnetic anisotropy can be interpreted to be the local properties of $4f$ electrons, namely, CEF effect. We can consider that this is also the case for $NdPd_5Al_2$, although the CEF level scheme has not been proposed yet. The Ising-type anisotropy is a common feature, which is also revealed in a recent study on high quality single crystals of $NdPd_5Al_2$.[11] This common feature can be interpreted from the unique crystal structure as in Fig. 1(a). The rare earth elements sandwiched by two Pd and Al ligand layers exhibit two dimensional nature with the $4f$ orbitals elongated within the c-plane. Consequently the wave functions with a flat orbital and large J_z become dominant. Thus the Ising anisotropy would be expected. Note the orbital moment is dominant in rare earth ions. In addition, a relatively large ordered moment of $NdPd_5Al_2$ as well as $CePd_5Al_2$ along the quantization axis of tetragonal c-axis can also be understood in a similar manner.

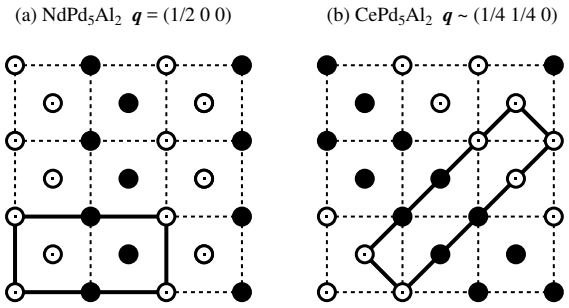

Fig. 5. The projection of the magnetic structure on to the tetragonal c-plane for (a) $NdPd_5Al_2$ and (b) $CePd_5Al_2$. The open and closed circles denote spin-up and -down, respectively. The dotted lines indicate chemical unit cell, while the solid lines denote magnetic one.

On the other hand, it is argued that the $NpPd_5Al_2$ with remarkable xy-type anisotropy is somehow different from the situation in the rare earth based reference compounds, which may be related to the unusual physical properties in $NpPd_5Al_2$;[10] for example, d-wave paring mediated by this xy-type magnetic fluctuation was pointed out by NMR studies.[3,4] However we can expect rather localized nature strongly remained in $NpPd_5Al_2$, because of the unique crystal structure with very large inter- and intra-plane distance between Np atoms. We need further study of $NpPd_5Al_2$ as well as iso-structural family to shed light on the electronic properties of f electron properties.

5. Conclusions

The magnetic structure of $NdPd_5Al_2$ was determined to propagation vector q=(1/2 0 0) and the Nd moment parallel to the c-axis similar to the one for $CePd_5Al_2$. In both cases the in-plane modulation can be understood by the two dimensional nature of fermi surface topology with dominant cylindrical fermi surfaces, which provides important information of the dynamical magnetic correlation in the heavy fermion superconductor $NpPd_5Al_2$.

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