Anomalous antiferromagnetic state in Nd$_2$Co$_{12}$P$_7$

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Abstract. We synthesized polycrystalline and single crystal samples of Nd$_2$Co$_{12}$P$_7$ and measured magnetization of the samples to study the antiferromagnetic ground state of this compound. We confirmed that Nd$_2$Co$_{12}$P$_7$ changes from the ferromagnetic state to the antiferromagnetic one with the decrease in temperature without magnetic phase transitions. In the antiferromagnetic state, the value of the Nd sublattice moment is 1.25 $\mu_B$ per Nd at $H = 0$, and it reaches the value of 2 $\mu_B$ in the saturating state achieved by a high magnetic field through a metamagnetic transition around 15 T. These values are smaller than the value expected for isolated Nd$^{3+}$ ions, although the magnetic moment of Nd ions behaves like that of isolated Nd$^{3+}$ ions in the paramagnetic state. The reason why the antiferromagnetic state realizes in the ferromagnetic state without magnetic phase transitions in Nd$_2$Co$_{12}$P$_7$ is that the internal magnetic field derived from the ferromagnetic Co sublattice gradually induces the Nd sublattice moment with decreasing temperature and the values of both sublattice moments become the same around the ground state.

1. Introduction

Localized magnetic moments in itinerant electronic ferromagnets can induce anomalous magnetic phenomena. The most prominent examples are base materials of permanent magnets LnCo$_5$, Ln$_2$Co$_7$ and Ln$_2$Fe$_{14}$B ($Ln =$ lanthanoids) etc. The spontaneous magnetization of the sublattice of the ferromagnetic transition metal in these materials is enhanced by localized magnetic moments of Ln in cases of light rare earth elements. Other examples are layered compounds LnCoPnO ($Pn = P, As$), which show ferromagnetic ordering of 3$d$ electrons of Co below the Curie temperature $T_C \sim 70$ K. Among LnCoPnO, anomalous antiferromagnetic states emerge in a low-temperature region of the ferromagnetic state in the cases of Ln = Nd, Sm, and Gd [1]. Although such antiferromagnetic transitions seem to be induced by localized magnetic moments of Ln [1], there have remained unsolved problems, e.g. the anomalous phase boundary between antiferromagnetic and ferromagnetic phases in the temperature-magnetic field plane [2] and an anomalous temperature dependence of the Ln sublattice moments [3]. For understanding such unusual magnetic phenomena, we need to study various itinerant electronic ferromagnets with localized magnetic moments.

For this purpose, we focused on itinerant ferromagnets Ln$_2$Co$_{12}$P$_7$, which have Zr$_2$Fe$_{12}$P$_7$-type crystal structure (space group : $P\bar{6}$) as shown in Fig. 1 [4]. In these compounds, 3$d$ electrons of Co show ferromagnetic ordering below $T_C \sim 150$ K. In the ferromagnetic state, the evolution of the spontaneous magnetizations with the drop of the temperature depends on Ln
\[ H/M = \left( \frac{N_A P_{\text{eff,Co}}^2}{3k_B(T - \theta_{\text{Co}})} + 2 \cdot \frac{N_A P_{\text{eff,Nd}}^2}{3k_B(T - \theta_{\text{Nd}})} \right)^{-1} \]
Figure 2. $T$ dependence of $H/M$ of the polycrystalline sample measured at 0.1 T. Black thin line is the result of fitting to Eq. (1).

by the least-squares method. $P_{\text{eff},X}$ is the effective Bohr magneton ($= g_J \mu_B \sqrt{J(J+1)}$, $g_J$ and $\mu_B$ are the Landé $g$-factor and the Bohr magneton, respectively) and $\theta_X$ is the Weiss temperature for $X$ ($X = \text{Nd or Co}$). The $k_B$ and $N_A$ are the Boltzmann constant and the Avogadro constant, respectively. Here, $P_{\text{eff},\text{Nd}}$ is held at the theoretical value of isolated Nd$^{3+}$ ($= 3.62 \mu_B$). As the result, we obtained values of the parameters as $\theta_{\text{Nd}} = - 25$ K, $P_{\text{eff},\text{Co}} = 1.09 \mu_B$, and $\theta_{\text{Co}} = 144$ K. Since these values are almost the same with those reported in Ref. [7], we think our analysis is reasonable. Our result shows two facts. One is that the energy scale of the crystal field that $4f$ electrons of Nd$^{3+}$ experience is small compared with $k_B T_C$. The other is that the interaction between the Nd and Co sublattices is negligible in the paramagnetic state.

Figure 3 shows $T$ dependence of $M$ of single crystals with $H$ applied along $c$-axis direction. Our results are consistent to those reported in Ref. [5]. We newly found that $M$ shows a difference between data measured after zero-field cooling (ZFC) and field cooling (FC) below 15 K. Since $M-T$ curves measured after ZFC and FC cross at 4 K and $M$ measured after ZFC takes negative values between 4 K and 10 K, Nd$_2$Co$_{12}P_7$ is in a similar state with compensated ferrimagnets in this temperature region. Although the detailed mechanism of such behavior is still unclear, it must be a key for understanding why antiferromagnetic state realizes at the ground state in Nd$_2$Co$_{12}P_7$.

Figure 4 shows $H$ dependence of $M$ of single crystals measured in steady field up to 12 T applied along $c$-axis direction. In the region between 75 to 135 K, $M-H$ curves show convex behaviors, which is typical of a ferromagnetic state. On the other hand, below 30 K, $M-H$ curves show linear or concave behaviors, which is indicative of a ferrimagnetic state. At 2 K, there is no spontaneous magnetization, showing Nd$_2$Co$_{12}P_7$ is in antiferromagnetic state. These results indicate that Nd$_2$Co$_{12}P_7$ changes from ferromagnetic to ferrimagnetic states with the decrease in temperature and is finally in the antiferromagnetic state at the ground state, but magnetic phase transition does not exist in each change.

Figure 5 shows a magnetization curve of single crystals with applying a pulsed magnetic field along $c$-axis direction at $T = 4.2$ K. We observed a metamagnetic transition around 15 T. Since at the zero field, both sublattice moments of Nd and Co align with the $c$-axis direction and are antiparallel with each other in this $T$-region, this transition is understood as that the relative direction between both sublattice magnetizations changes from antiparallel to parallel with the increase in the magnetic field. From the value of $M$ above 30 T, we estimated the saturating magnetization of Nd$_2$Co$_{12}P_7$ as about 8 $\mu_B$ per formula unit.
Figure 3. (a) $T$ dependence of $M$ of single crystals of Nd$_2$Co$_{12}$P$_7$ measured at $H = 0.1$ T and 5 T. $H$ is applied along $c$-axis of single crystals. (b) Magnification of panel (a) in the region of $T \leq 25$ K.

Figure 4. Magnetization curves measured at various temperatures in the $T$-range of (a) $T \leq 30$ K and (b) 75 K $\leq T \leq 135$ K. $H$ is applied along $c$-axis of single crystals.

We discuss the value of the Nd sublattice moment in the antiferromagnetic state. From the Fig. 4 (b), one can estimate the spontaneous magnetization at 75 K as 2.3 $\mu_B$ per formula unit. Since Nd$_2$Co$_{12}$P$_7$ is in the ferromagnetic state in this temperature region, the spontaneous magnetization must correspond to the Co sublattice moment. By a natural extrapolation to zero temperature, we roughly estimated the Co sublattice moment at the ground state as 2.5 $\mu_B$ per formula unit. In the ground state, the Nd sublattice moment is in antiparallel with the Co sublattice moment, and the value of it is the same with that of the Co sublattice moment. Therefore, the Nd sublattice moment at the ground state is 1.25 $\mu_B$ per Nd. This value is smaller than the theoretical value expected for an isolated Nd$^{3+}$ ion (= 3.27 $\mu_B$). We also estimated the value of the Nd sublattice moment in the high-$H$ region. As stated above, the value of the saturating magnetization is about 8 $\mu_B$ per formula unit. In the previous report, the value of the saturating magnetization of Lu$_2$Co$_{12}$P$_7$ is 4 $\mu_B$ per formula unit [5]. If the
Figure 5. Magnetization curve at 4.2 K. $H$ is applied along $c$-axis of single crystals.

The saturating magnetization of the Co sublattice is the same among $Ln_2Co_{12}P_7$, we can estimate the Nd sublattice moment as 4 $\mu_B$ per formula unit by subtracting the value of the Co sublattice moment from the saturating magnetization. As a result, the value of the Nd sublattice moment is 2 $\mu_B$ per Nd in the high-$H$ region. This value is larger than the value for the low-$H$ region (1.25 $\mu_B$ per Nd) but is still smaller than the theoretical value for an isolated Nd$^{3+}$ ion.

In the case of $Ln_2Co_{12}P_7$, the electronic state of $Ln^{3+}$ is reported to be well explained by the effective Hamiltonian $\hat{H}_{\text{eff}}$ as described by the following equation [6],

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{cfe}} + \lambda \hat{S} \cdot \hat{L} + \alpha \hat{H}_{\text{ex}} \cdot \hat{S}, \quad (2)$$

where the first and second terms correspond to crystal field effect and spin-orbital coupling, respectively. The third term corresponds to coupling between the spin part of $4f$ electrons and the exchange field ($H_{\text{ex}}$) derived from the ferromagnetic sublattice. The $\lambda$ is the spin-orbital coupling constant. It has been succeeded in explaining a electronic state of $Ln^{3+}$ in the base materials of permanent magnet by Eq. (2) [8]. Here, the constant $\alpha$ is equal to $+2$ in case of permanent magnet [8], and is less than zero in case of $Ln_2Co_{12}P_7$ [6]. Therefore, the spin part of magnetic moment of $Ln^{3+}$ tends to align in parallel with $H_{\text{ex}}$ in the case of $Ln_2Co_{12}P_7$. As a result, the total magnetic moment of Nd ions aligns in antiparallel with the ferromagnetic Co sublattice moment since $\lambda > 0$ in the case of Nd. Figure 6 schematically shows how magnetic moments are coupled each other. In the paramagnetic state, $4f$ electrons of Nd$^{3+}$ are expected to be in the same state with the isolated one, whose magnetic moment is $g_JJ = 3.27 \mu_B$. However, below 5 K, the Nd sublattice moment is smaller than the expected value from the value of $g_JJ$ of an isolated Nd$^{3+}$ ion in both the low-$H$ and high-$H$ regions. Also, the temperature dependence of the Nd sublattice moment is anomalous as seen in Fig. 3 (a). These unusual behaviors can be understood by the model as following. In the Nd sublattice, where each Nd$^{3+}$ has the same value of magnetic moment with that of isolated Nd$^{3+}$ ions, ordered moments on Nd sites are gradually induced by $H_{\text{ex}}$ of the Co sublattice with decreasing temperature. The induced moments of Nd$^{3+}$ ions finally cancel the Co sublattice moment below 5 K. For now, we do not know whether there is a necessity for the complete cancellation of sublattice moments at the ground state or not. It is also possible that magnetic moments of Nd$^{3+}$ ions take a smaller value in the low-$T$ region compared with the value in the paramagnetic state due to the crystal field splitting of the lowest energy term $^4I_{9/2}$. To understand anomalous magnetism of Nd$_2$Co$_{12}$P$_7$, further studies are needed.
Figure 6. Schematic explanation of interaction between the ferromagnetic Co sublattice moment ($S_{3d}$) and the spin part of the magnetic moment ($S_{4f}$) and the orbital part of the magnetic moment ($L_{4f}$) of Nd$^{3+}$.

4. Conclusion
We synthesized polycrystalline and single crystal samples of Nd$_2$Co$_{12}$P$_7$ and measured magnetization of the samples. We observed a gradual increase of the Nd sublattice moment with decreasing temperature, which is quite different from the temperature dependence of ordered moments in an ordinary two-sublattice model. Also, we newly observed anomalous hysteresis in the temperature dependence of magnetization below 15 K which reminds us compensated ferrimagnets, although Nd$_2$Co$_{12}$P$_7$ is in the antiferromagnetic state in the ground state. In the antiferromagnetic state, we confirmed that the Nd sublattice moment takes a smaller value than the value expected for isolated Nd$^{3+}$ ions. We suggested that anomalous behavior of the Nd sublattice moment is due to the coupling between localized magnetic moments of Nd ions and a ferromagnetic exchange field.

Acknowledgments
This work was supported by Grants-in-Aid for Young Scientists (B) from Japan Society for the Promotion of Science (Grant Nos. 24760534 and 15K18211).

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