Anomalous Behavior of Localized Magnetic Moments in Itinerant Ferromagnets

$Ln_2Co_{12}P_7$ \( (Ln = Y, Pr, Nd, Sm, Gd and Dy) \)

Hiroto OHTA$^{1,*}$, Yusuke WATANABE$^1$, Atsushi MIYAKE$^2$, Masashi TOKUNAGA$^2$ and Hiroko ARUGA KATORI$^1$

$^1$Department of applied physics, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Koganei 184-8588, Japan.

$^2$Institute for Solid State Physics, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8581, Japan.

Received November 30, 2015; Revised February 18, 2016; Accepted February 22, 2016

ABSTRACT

We synthesized polycrystalline samples of ternary compounds $Ln_2Co_{12}P_7$ \( (Ln = Y, Pr, Nd, Sm, Gd and Dy) \) with the Curie temperature being about 150 K and measured magnetization to clarify magnetcism of Co sublattice and also to clarify behavior of magnetic moments of $Ln^{3+}$ in ferromagnetic phase. As a result, magnetism of $Y_2Co_{12}P_7$ was found to be a possible weakly itinerant electronic ferromagnetism and found to be similar to that of $Lu_2Co_{12}P_7$, indicating that magnetism of Co sublattice does not change with $Ln$. From results for $Ln_2Co_{12}P_7$, we found that spin components of magnetic moments of $Ln^{3+}$ ferromagnetically couple with exchange field of ferromagnetic moments of Co sublattice. This result means that behavior of magnetic moments of $Ln^{3+}$ can be described as the single ion model applied to the permanent magnets ($LnCo_3$, $Ln_2Fe_14B$ etc.) though the sign of coupling constant is opposite of the cases of permanent magnets. This is because magnetic moments of Co and $Ln$ couple through P, not a direct coupling in cases of permanent magnets.

KEY WORDS

$Ln_2Co_{12}P_7$, itinerant electronic ferromagnetism, ternary compound

1 Introduction

Ternary lanthanoid transition metal pnictides have much variety of compounds with different crystal structure and thus have much variety of physical properties. For example, in the $LnM_2Pn_3$ system which is well known as the filled Skutterudite, physical property is ranging from unconventional superconductivity to anomalous thermal conductivity because of rattling motions of $Ln$. Here, $Ln$ is lanthanoids, $M$ is transition metal elements and $Pn$ is pnictogen elements. $Ln_2M_2Pn_3$ system is one of such ternary systems and has $Zr_2Fe_2P_7$-type crystal structure (hexagonal, space group: P-6) as shown in Fig. 1. The crystal structure of $Ln_2M_2Pn_3$ can be seen as a filled $Cr_{12}P$ structure$^{13}$, reminding us of the case of the filled Skutterudite. Actually, all the lanthanoid elements except La, Y, Sc and tetravalent ions of Zr and Ti are reported to occupy the $Ln$ site$^{19}$, indicating that the $Ln$ site is in a robust cage of phosphorous atoms as the case of the Skutterudite. For this reason, the $Ln_2M_2Pn_3$ system has aroused interest for a long time and intensive studies have been devoted.

Magnetic properties of the $M$ sublattice of $Ln_2M_2Pn_3$ have been studied, and it is revealed that the $M$ sublattice shows the Pauli paramagnetism in the cases of $M = Fe$ and Ni while it shows ferromagnetism with the Curie temperature of $T_C \sim 150$ K in the case of $M = Co^{6,7}$. Therefore, from a view point of itinerant electronic magnetism $Ln_2Co_{12}P_7$, the most important compounds in the $Ln_2M_2Pn_3$ system. For now, magnetism of several compounds have been studied and anomalous magnetic properties have been reported$^{6,8}$. For example, $Nd_2Co_{12}P_7$, shows antiferromagnetic ordering at low temperature without any phase transition from ferromagnetic state with decreasing temperature. For understanding magnetic properties of the $Ln_2Co_{12}P_7$ system, systematic study on $Ln$ dependence of magnetism is necessary. However, such a systematic study has been done only on paramagnetic state$^{6}$, and thus anomalous magnetism in ordered state has not been fully understood.

In this paper, we synthesized polycrystalline samples of $Ln_2Co_{12}P_7$ with $Ln = Y, Pr, Nd, Sm, Gd and Dy$ and measured magnetization of the samples to systematically study magnetism of the $Ln_2Co_{12}P_7$ system in ordered state.

2 Experiments

Polycrystalline samples of $Ln_2Co_{12}P_7$ were synthesized by a solid state reaction method. Powder of $Ln$ \( (Ln = Y, Ce, Pr, Nd, Sm, Gd or Dy) \) (purity: 99.9 %), Co (99.9 %) and P (99.9999 %) were mixed and then heated at 1,273 K for 12 hs in evacuated silica tubes. Obtained samples were well ground and fired at 1,473 K for 12 hs in vacuum.

* Corresponding author, E-mail: h-ohta@cc.tuat.ac.jp
Anomalous Behavior of Localized Magnetic Moments in Itinerant Ferromagnets \( Ln_2Co_{12}P_7 \) (\( Ln = Y, Pr, Nd, Sm, Gd \) and Dy)

Evacuated silica tubes. Samples were characterized by using powder X-ray diffraction (XRD) measurements with Cu \( K_\alpha \) radiation. Magnetization (\( M \)) of samples were measured by using vibrating sample magnetometer (MagLab™, Oxford) and also measured by using a non-destructive pulse magnet installed in Institute for Solid State Physics, the University of Tokyo up to 56 T.

3 Results and Discussion

Fig. 2 (a) shows results of powder XRD measurements of \( Ln_2Co_{12}P_7 \) for \( Ln = Y, Pr, Nd, Sm, Gd \) and Dy. Red and blue data are obtained and simulated patterns, respectively. These simulated patterns are obtained from calculation by using lattice parameters estimated from the experimental patterns. Good agreement of the experimental pattern with the simulated one for each sample indicates that samples are in a single phase of \( Ln_2Co_{12}P_7 \). Fig. 2 (b), 2 (c) and 2 (d) show lattice parameters \( a \), \( c \) and cell volume \( V \) of \( Ln_2Co_{12}P_7 \), respectively.

By choosing nonmagnetic lanthanoids as \( Ln \), we can study magnetic property of Co sublattice in detail. For understanding of magnetism of Co sublattice in \( Ln_2Co_{12}P_7 \) system, it is also important to study magnetic property of \( Y_2Co_{12}P_7 \). Fig. 3 (a) shows temperature (\( T \)) dependence of \( M \) measured after field cooling (FC) and zero field cooling (ZFC) under magnetic field (\( H \)) = 0.1 T and \( T \) dependence of \( H/M \) measured under \( H = 1 \) T. In the paramagnetic state, \( H/M \) shows a linear behavior, indicating that magnetic moments of Co obey the Curie Weiss law. As the result of fitting, we estimated magnetic parameters, i.e. the effective Bohr magneton number \( P_{\text{eff}} \) and the Weiss temperature \( \theta \), of magnetic moments of Co as \( P_{\text{eff}} = 1.18 \) per Co and \( \theta = 158 \) K. Fig. 3 (b) shows isothermal magnetizations of \( Y_2Co_{12}P_7 \) measured at various temperatures. At \( T = 2 \) K, there is observed hysteresis loop below \( H = 1.7 \) T. This is consistent with divergence between ZFC and FC observed in \( T \) dependence of \( M \) below 140 K. Such hysteresis loop in magnetization curve was also reported in the case of \( Ln = Lu \). We estimated spontaneous magnetization at \( T = 2 \) K as \( P_s = 0.14 \mu_B/\text{Co} \). Spontaneous magnetization becomes zero at \( T = 156 \) K, so the Curie temperature is determined as \( T_c = 156 \) K. The estimated values of magnetic parameters are listed in Table 1. The parameters for \( Y_2Co_{12}P_7 \) are almost the same with those for \( Lu_2Co_{12}P_7 \) reported in
It is noteworthy that the ratio of $P_{\text{eff}}$ and $P_s$ for Co sublattice of $\text{Ln}_2\text{Co}_{12}\text{P}_7$ system is about 8, indicating shrinkage of ordered moments due to spin fluctuations. In the theory for itinerant electronic ferromagnetism by Takahashi, $P_{\text{eff}}/P_s$ is related to $T_C/T_0$ as $P_{\text{eff}}/P_s = 1.4 \left( T_C/T_0 \right)^{-2/3}$ for the three-dimensional case. Here, $T_0$ characterizes the energy width of the dynamical spin fluctuation spectrum. From this relation, $T_C/T_0$ is estimated as 0.068 and then $T_0$ is estimated as 2300 K. Since this value is reasonable compared with intermetallic ferromagnets, $T_0$ can be estimated from the slope of $M^4$ versus $H/M$ at $T = T_C$ if $M^4$ shows a linear relation with $H/M$. For the case of $\text{Y}_2\text{Co}_{12}\text{P}_7$, unfortunately, $M^4$ does not show such a linear relation with $H/M$, which is thought to be due to magnetic anisotropy. For further precise analysis, study using single crystals is needed.

Fig. 4 shows temperature dependence of magnetization measured at $H = 0.1$ T. The data of $\text{Ho}_2\text{Co}_{12}\text{P}_7$ are reproduced from Ref.\(^6\) which were measured at $H = 0.2$ T.

Table 1 Magnetic parameters for $\text{Ln}_2\text{Co}_{12}\text{P}_7$ ($\text{Ln} = \text{Y}$ or Lu): the spontaneous magnetization per Co at the lowest temperature $P_s$ in unit of $\mu_B$, the effective Bohr magneton number per Co $P_{\text{eff}}$, the Weiss temperature $\theta$ and the Curie temperature $T_C$.

<table>
<thead>
<tr>
<th>$\text{Ln}$</th>
<th>$P_s$ ($\mu_B$)</th>
<th>$P_{\text{eff}}$</th>
<th>$\theta$ (K)</th>
<th>$T_C$ (K)</th>
<th>$P_{\text{eff}}/P_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}$</td>
<td>0.14</td>
<td>1.18</td>
<td>158</td>
<td>156</td>
<td>8.43</td>
</tr>
<tr>
<td>$\text{Lu}$</td>
<td>0.15</td>
<td>1.14</td>
<td>158</td>
<td>150</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Fig. 3 (a) $T$ dependence of $M$ of $\text{Y}_2\text{Co}_{12}\text{P}_7$ at $H = 0.1$ T and $H/M$ at $H = 1$ T. Solid line is a result of the Curie Weiss fitting. (b) Isothermal magnetizations of $\text{Y}_2\text{Co}_{12}\text{P}_7$ at various temperatures.

Refs.\(^6\)\(^9\), showing that magnetism of Co sublattice in $\text{Ln}_2\text{Co}_{12}\text{P}_7$ is almost independent of $\text{Ln}$.

It is noteworthy that the ratio of $P_{\text{eff}}$ and $P_s$ for Co sublattice of $\text{Ln}_2\text{Co}_{12}\text{P}_7$ system is about 8, indicating shrinkage of ordered moments due to spin fluctuations. In the theory for itinerant electronic ferromagnetism by Takahashi, $P_{\text{eff}}/P_s$ is related to $T_C/T_0$ as $P_{\text{eff}}/P_s = 1.4 \left( T_C/T_0 \right)^{-2/3}$ for the three-dimensional case. Here, $T_0$ characterizes the energy width of the dynamical spin fluctuation spectrum. From this relation, $T_C/T_0$ is estimated as 0.068 and then $T_0$ is estimated as 2300 K. Since this value is reasonable compared with intermetallic ferromagnets, $T_0$ can be estimated from the slope of $M^4$ versus $H/M$ at $T = T_C$ if $M^4$ shows a linear relation with $H/M$. For the case of $\text{Y}_2\text{Co}_{12}\text{P}_7$, unfortunately, $M^4$ does not show such a linear relation with $H/M$, which is thought to be due to magnetic anisotropy. For further precise analysis, study using single crystals is needed.

Fig. 4 shows temperature dependence of magnetization measured at $H = 0.1$ T: Fig. 4 (a) is for compounds with $\text{Ln} = \text{Y}$, $\text{Pr}$, $\text{Nd}$, $\text{Sm}$, $\text{Gd}$ and $\text{Dy}$) measured after field cooling at $H = 0.1$ T. The data of $\text{Ho}_2\text{Co}_{12}\text{P}_7$ are reproduced from Ref.\(^13\) which were measured at $H = 0.2$ T.

Table 1 Magnetic parameters for $\text{Ln}_2\text{Co}_{12}\text{P}_7$ ($\text{Ln} = \text{Y}$ or Lu): the spontaneous magnetization per Co at the lowest temperature $P_s$ in unit of $\mu_B$, the effective Bohr magneton number per Co $P_{\text{eff}}$, the Weiss temperature $\theta$ and the Curie temperature $T_C$.

<table>
<thead>
<tr>
<th>$\text{Ln}$</th>
<th>$P_s$ ($\mu_B$)</th>
<th>$P_{\text{eff}}$</th>
<th>$\theta$ (K)</th>
<th>$T_C$ (K)</th>
<th>$P_{\text{eff}}/P_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}$</td>
<td>0.14</td>
<td>1.18</td>
<td>158</td>
<td>156</td>
<td>8.43</td>
</tr>
<tr>
<td>$\text{Lu}$</td>
<td>0.15</td>
<td>1.14</td>
<td>158</td>
<td>150</td>
<td>7.60</td>
</tr>
</tbody>
</table>
heavy rare earth. Such a coupling has been reported in the cases of permanent magnets \( LnCo_7, LnCo_9 \) and \( LnFe_7B \), though the sign of coupling constant is opposite of the case for \( LnCo_9P_7 \): for the case of light rare earth elements, the values of \( M \) are larger, and for the case of heavy rare earth elements, the values of \( M \) are smaller for the cases of those permanent magnets. In the model for these permanent magnets\(^{12} \), localized magnetic moments of \( Ln^{3+} \) couple with ferromagnetic moments of transition metals through the term of Hamiltonian \( H = 2 \mathbf{H}_c \cdot \mathbf{S} \), where \( \mathbf{H}_c \) is an exchange field from \( 3d \) electrons of transition metals and \( \mathbf{S} \) is spin component of \( 4f \) electrons. In this model, since spin components of \( 4f \) electrons align antiparallel to ferromagnetic moments of transition metals, magnetic moments of \( Ln^{3+} \) electrons couple with ferromagnetic moments as shown above. \( LnCo_9P_7 \), can be understood as similar model but sign of the term of Hamiltonian above is opposite. The difference of sign of the term is thought to originate from whether lanthanoids directly form chemical bonds with transition metals or not. In the case of \( LnCo_9P_7 \), a possible scenario is that ferromagnetic split of \( 3d \) band of \( Co \) induces magnetic moments on \( 3p \) band of \( P \) in antiparallel with ferromagnetic moments of \( Co \) and then these magnetic moments on \( 3p \) band induces magnetic moments on \( 5d \) band of \( Ln \) in antiparallel with magnetic moments on \( P \). This is just a speculation, and theoretical approaches are expected for further understanding.

As shown in Fig. 4, divergence between \( M \) of \( LnCo_9P_7 \), and that of \( YCo_9P_7 \), enhances with decreasing temperature. Taking into account the fact that ferromagnetic magnetization of Co sublattice, or \( H_c \), does not develop so much below 100 K, thermal average of magnetic moments of \( Ln^{3+} \) is thought to develop with decreasing temperature as if magnetization which weakly induced by external magnetic field in paramagnetic states develops by obeying the Curie Weiss law with decreasing temperature. This is more evident in anomalous temperature dependence of intensity of peaks of neutron diffraction measured for the cases of \( Ln = Nd \), \( Ho \) and \( Tb \).

Fig. 5 shows isothermal magnetization curves measured at \( T = 1.4 \) K. For the case of \( Ln = Y \), saturation magnetization is \( 3.7 \mu_B \) per formula unit, showing that saturation magnetization of Co sublattice can be regarded as \( 3.7 \mu_B \) for all the cases of \( LnCo_9P_7 \). Therefore, if magnetic moments of \( Ln^{3+} \) are forced to align parallel to magnetic moments of Co sublattice by external magnetic field, saturation magnetization is expected to reach the value of \( M_{sat} = (3.7 + 2g_J) \mu_B \) where \( g_J \) is the Lande \( g \)-factor and \( J \) is total angular momentum. The factor “2” of the second term is number of \( Ln \) atoms in formula unit. The expected values of \( g_J \) and \( M_{sat} \) for isolated \( Ln^{3+} \) ions are listed in Table 2. As seen in Fig. 5 (b), \( M \) of \( GdCo_9P_7 \) easily reached the value of \( M_{sat} \) for isolated ions, and for the case of \( DyCo_9P_7 \), \( M \) seemed to approach the value of \( M_{sat} \) for the isolated ion with increasing \( H \). In addition, for the case of \( HoCo_9P_7 \), there has been reported that \( M \) reaches \( 14 \mu_B \) per formula unit at \( H = 5 \) T and \( T = 5 \) K\(^0 \). If \( Ho^{3+} \) ion is isolated from environment, \( g_J = 10 \) and thus \( M_{sat} = 23.7 \mu_B \) as the case of \( Dy \). Therefore, \( M \) of \( HoCo_9P_7 \) also seems to approach the value of \( M_{sat} \) for isolated ion as \( DyCo_9P_7 \). For the cases of \( Ln = Dy \), \( M \) rather gradually increases with \( H \) compared with the case of \( Ln = Gd \), which is possibly due to anisotropic nature of these ions.

On the other hand, the cases of light rare earth elements \( Ln \) dependence of magnetic curves are a little bit complicated compared with the cases of heavy ones. For the cases of \( Ln = Pr \) and \( Nd \), as

![Fig. 5](image-url)  

---

**Table 2** Values of \( gJ \) and \( M_{sat} \) of \( LnCo_9P_7 \), with \( Ln = Pr, Nd, Sm, Gd \) and \( Dy \) in the assumption that \( Ln^{3+} \) ions are isolated from their surroundings. \( M_{sat} \) is per formula unit and in unit of \( \mu_B \).

<table>
<thead>
<tr>
<th>( Ln )</th>
<th>( Pr )</th>
<th>( Nd )</th>
<th>( Sm )</th>
<th>( Gd )</th>
<th>( Dy )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_J )</td>
<td>16/5</td>
<td>36/11</td>
<td>5/7</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>( M_{sat} )</td>
<td>10.1</td>
<td>10.2</td>
<td>5.1</td>
<td>17.7</td>
<td>23.7</td>
</tr>
</tbody>
</table>
shown in Fig. 5 (a), $M$ is larger than that of $Ln = Y$ in the range of $H >$ about 15 T. Since the cases of light rare earth elements, magnetic moments of $Ln^{3+}$ couple in antiparallel with those of Co sublattice and as a result $M$ of $Ln_2Co_{12}P_7$ is smaller than that of $Y_2Co_{12}P_7$, the larger value of $M$ observed above 15 T indicates that magnetic moments of $Ln^{3+}$ flip and align parallel to those of Co sublattice in some degree. Both the cases of $Ln = Pr$ and Nd, $M$ almost saturates around $H = 60$ T, where the values of $M$ are 5 $\mu_B$ for Pr and 7.3 $\mu_B$ for Nd. From these values, magnetic moments of $Pr^{3+}$ and $Nd^{3+}$ are estimated as 0.6 $\mu_B$ for Pr and 1.8 $\mu_B$ for Nd. These values are smaller than the values of $g_J \mu_B$ for isolated ions. The shrinkage of magnetic moments possibly originates in anisotropy of $4f$ electrons. It is also possible that such shrinkage is related with the fact that in the low-$H$ region magnetic moments of $Ln^{3+}$ are induced by the exchange field. For the case of $Ln = Sm$, there is no sign of spin-flip up to $H = 56$ T but is just a gradual increase of $M$ against $H$ in contrast to the cases of $Ln = Pr$ and Nd. Energy of field induced magnetic transition like spin-flip or metamagnetic ones is related to both anisotropy and Zeeman energies, and the latter is closely related with size of magnetic moments. Therefore, character of magnetization curve of Sm$_2$Co$_{12}P_7$ is possibly understood by large anisotropy energy and/or smaller size of magnetic moments of Sm$^{3+}$.

From the results of magnetic measurements, behavior of magnetic moments of $Ln^{3+}$ in $Ln_2Co_{12}P_7$, is found to be roughly understood by the single ion model applied to the permanent magnets. However, our discussion above lacks consideration of anisotropy of magnetic moments of $Ln^{3+}$ ions. Usually, the ground state of $4f$ electrons for the case of $Ln^{3+}$ ions well isolated from environments splits by the effect of crystal field and thus size of magnetic moments and their anisotropy change depending on the true ground state. Therefore, information about the ground state of $Ln^{3+}$ with taking crystal field effects into account is necessary for further understanding.

4 Conclusion

In summary, we synthesized polycrystalline samples of $Ln_2Co_{12}P_7$, with $Ln = Y$, Pr, Nd, Sm, Gd and Dy, and measured magnetization of these compounds. We confirmed that magnetic property of $Y_2Co_{12}P_7$ is quite similar to that of $Lu_2Co_{12}P_7$, indicating that magnetic property of Co sublattice is common in all the $Ln_2Co_{12}P_7$. We also pointed out that magnetism of Co sublattice is possibly categorized as weakly itinerant ferromagnetism. Magnetism of $Ln$ sublattice can be understood by the single ion model applied to permanent magnets, though the sign of coupling constant between magnetic moments of $Ln^{3+}$ and exchange field derived from Co sublattice is opposite.

Acknowledgments

This work was supported by Grant-in-Aid for Young Scientists (B) from Japan Society for the Promotion of Science (Grant No. 24760534).

References

5) W. Jeitschko, U. Meisen, E. J. Reinbold: “Scandium as an Element Intermediate between Rare Earth and Transition Metals in Intermetallics: Crystal Structure of $Sc_2Fe_{12}P_7$, $Sc_3Fe_{10}P_7$, and $Sc_2Co_{12}P_7$. Other New Compounds with $Zr_2Fe_{12}P_7$, $Hf_2Co_{12}P_7$, $Sc_2Co_{12}P_7$, and $Yb_2Co_{12}P_7$ Type Structures”, Z. Anorg. Allg. Chem., 638 (2012) 770.