NMR study of filled skutterudite NdOs$_4$P$_{12}$

K. Magishi, K. Nagata, Y. Iwahashi, H. Sugawara, T. Saito and K. Koyama
Institute of Socio-Arts and Sciences, The University of Tokushima, Tokushima 770-8502, Japan
E-mail: magishi@ias.tokushima-u.ac.jp

Abstract. We have succeeded in growing the single crystals of NdOs$_4$P$_{12}$ and investigated the electrical resistivity, magnetic susceptibility and nuclear magnetic resonance (NMR). NdOs$_4$P$_{12}$ shows metallic behavior in the electric resistivity and undergoes a ferromagnetic transition at 1.15 K. The Knight shift increases upon cooling, similar to the magnetic susceptibility, and little depends on the magnetic field except for below 10 K. Also, the nuclear spin-lattice relaxation rate divided by temperature $1/T_1T$ is largely enhanced with decreasing temperature, implying the significant development of the magnetic fluctuations. $1/T_1T$ is strongly suppressed by the magnetic field, in contrast to the Knight shift. It suggests the coexistence of the ferromagnetic and antiferromagnetic spin fluctuations, similar to the results for NdRu$_4$P$_{12}$.

1. Introduction

The family of filled skutterudites with the general formula $RM_4X_{12}$ ($R =$ lanthanides etc., $M =$ Fe, Ru, Os, $X =$ P, As, Sb) has attracted a great deal of interest. This is not only due to their promising thermoelectric properties, but also because these compounds show a wide variety of transport and magnetic properties at low temperatures, such as superconductivity, magnetic ordering, the heavy-fermion state, metal-insulator transition and semiconducting transport. Among them, all of the Nd-based filled skutterudites show the ferromagnetic (FM) ordering, which suggests that the intersite interaction between Nd$^{3+}$ ions tends to be ferromagnetic in the filled skutterudites. As for NdOs$_4$P$_{12}$, there are no reports of physical properties, except for lattice constants. Recently, we have succeeded in growing the single crystals of NdOs$_4$P$_{12}$.

In this paper, we report on the electrical resistivity, magnetic susceptibility and nuclear magnetic resonance (NMR) for filled skutterudite NdOs$_4$P$_{12}$ to deepen the understanding of the electronic states at low temperatures. NMR is a powerful tool to investigate the magnetic properties from microscopic viewpoints.

2. Experimental

Single crystals of NdOs$_4$P$_{12}$ were synthesized using the tin-flux method from a mixture of elemental Nd(4N), Os(4N), P(6N) and Sn(5N) in a ratio of 1:4:20:50. The electrical resistivity was measured by the conventional DC four probe method in the home made $^3$He cryostat down to 0.4 K. The magnetic susceptibility was measured by the SQUID magnetometer MPMS XL-7 (Quantum Design). The samples were crushed into powder for the NMR measurements. The NMR measurements were performed in a temperature range between 1.5 K and 300 K using a conventional phase-coherent pulsed spectrometer. The NMR spectrum was obtained by
integrating spin-echo with sweeping magnetic field. The nuclear spin-lattice relaxation time $T_1$ was measured by the saturation recovery method.

3. Results and Discussion

3.1. Electrical Resistivity

Figure 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ normalized at 300 K for NdOs$_4$P$_{12}$. As seen in the inset, the $\rho(T)$ curve shows a broad minimum near 20 K, followed by a logarithmical increase, which is attributed to the Kondo effect. This behavior is similar to that of NdFe$_4$P$_{12}$[1, 2, 3], which is quite unusual for FM materials. Upon cooling, $\rho(T)$ exhibits a sharp drop at $\sim 1.15$ K, which is associated with the onset of magnetic ordering. The residual resistivity ratio (RRR) is $\sim 100$ for NdOs$_4$P$_{12}$. The $4f$ component $\rho_{4f}$ in NdOs$_4$P$_{12}$ (not shown), where the phonon part of $\rho(T)$ is subtracted using the data of LaOs$_4$P$_{12}$[4], decreases gradually with decreasing temperature below $\sim 150$ K, which may be ascribed to the decreasing of magnetic scattering associated with the crystalline electric field (CEF) excitation.

3.2. Magnetic Susceptibility

Figure 2 shows the temperature dependencies of the magnetic susceptibility $\chi(T)$ for NdOs$_4$P$_{12}$ at several magnetic fields. $\chi(T)$ is enhanced at low temperature, and is largely suppressed by applying magnetic field below 10 K. This behavior is a characteristic of ferromagnetic ordering. As seen in the inset, the $\chi^{-1}(T)$ data exhibit different slopes at high and low temperatures. The linear slope of $\chi^{-1}(T)$ between 50 K and 300 K yields a Weiss temperature $\Theta_W = -23$ K and an effective moment $\mu_{\text{eff}} = 3.03 \mu_B$, which is slightly smaller than the Nd$^{3+}$ free-ion value of 3.62 $\mu_B$, as shown in the inset of Fig.2. $\chi^{-1}(T)$ deviates from the linear slope at high temperatures and decreases with decreasing temperature exhibiting a broad hump around 50 K. Assuming the CW law at low temperature below 10 K, $\mu_{\text{eff}} = 2.34 \mu_B$ and $\Theta_W = 1.0$ K are estimated in the $T \rightarrow 0$ K limit. The curvature in $\chi^{-1}(T)$ is due to the influence of the CEF, and the positive $\Theta_W$ from the low-temperature fit indicates ferromagnetic order developing below 1 K. The negative $\Theta_W$ changes its sign at low temperatures, implying a presence of both FM and antiferromagnetic (AFM) exchange interactions.
3.3. NMR

The $^{31}$P NMR spectrum shows the uniaxially symmetric powder pattern due to anisotropic Knight shift. The Knight shift components perpendicular $K_\perp$ and parallel $K_\parallel$ to the principal axis are derived from the peak maximum and the shoulder peak in the spectra, respectively. Figure 3 shows the temperature dependencies of $K_\perp$ and $K_\parallel$ for NdOs$_4$P$_{12}$. At low temperatures below 4 K, it is difficult to determine the Knight shift component $K_\parallel$ due to the broadening of the spectrum. The Knight shift increases upon cooling, similar to that of the magnetic susceptibility, and little depends on the magnetic field except for 10 K. Similar behavior was observed in NdRu$_4$P$_{12}$[5].

Inset displays the $K - \chi$ plots in magnetic field at 1.2 T, where both components of the Knight shift are plotted against the magnetic susceptibility with the temperature as an implicit parameter. Both have linear relations with the susceptibility. From these linear relations, the components of the hyperfine coupling constant on $^{31}$P nuclei are estimated as $A_\parallel = 1.3$ kOe/$\mu_B$ and $A_\perp = 0.2$ kOe/$\mu_B$ for NdOs$_4$P$_{12}$. The hyperfine fields are also expressed using the isotropic and anisotropic components as $A_{\text{iso}} = (A_\parallel + 2A_\perp)/3 = 0.57$ kOe/$\mu_B$ and $A_{\text{aniso}} = (A_\parallel - A_\perp)/3 = 0.37$ kOe/$\mu_B$ for NdOs$_4$P$_{12}$. The positive isotropic component $A_{\text{iso}}$ arises from the Fermi-contact interaction between the P-4s orbital and the Nd-4f spins, while the anisotropic component $A_{\text{aniso}}$ is ascribed to the dipolar interaction.

Figure 4 indicates the temperature dependencies of the nuclear spin-lattice relaxation rates divided by temperature $1/T_1T$ for $^{31}$P nuclei in NdOs$_4$P$_{12}$ measured at several magnetic fields. $1/T_1T$ is largely enhanced with decreasing temperature, implying the significant development of the magnetic fluctuations. As further decreasing temperature, $1/T_1T$ decreases with a peak, which is attributed to the suppression of FM fluctuations. Also, in contrast to the result of the Knight shift, $1/T_1T$ strongly depends on the magnetic field. The peak shifts to higher temperature with increasing field, similar to the result of NdRu$_4$P$_{12}$[5].

Generally, $1/T_1T$ is expressed as

$$\frac{1}{T_1T} \propto \lim_{\omega \to 0} \sum_q |A_q|^2 \frac{\chi''(q, \omega)}{\omega}$$

where $\chi''(q, \omega)$ is the imaginary part of the dynamical susceptibility. Since $K_s$ and $1/T_1T$ probes $\chi_s = \chi(0, 0)$ and $\sum_q \chi(q, \omega \to 0)$, $1/T_1T$ is enhanced by either FM or antiferromagnetic (AFM)
correlations, while $K_s$ is enhanced by only FM correlations. When both $K_s$ and $1/T_1 T$ are due to the hyperfine field from $s$ electrons for non-interacting electron systems such as simple metals, the Korringa relation is known to be satisfied as $T_1 TK_s^2 = (\gamma_e/\gamma_n)^2 (h/4\pi k_B) \equiv S$. In the presence of interactions, the ratio $R \equiv S/T_1 TK_s^2$ provides a useful measure of magnetic correlations, where the value of $R$ smaller (larger) than unity is a signature for the presence of FM (AFM) correlations. As seen in the inset, the value of $R$ becomes larger than unity with decreasing temperature, pointing to the AFM enhancement.

As mentioned above, the Knight shift is almost independent of the magnetic field above 10 K, implying that $\chi(0,0)$ is insensitive to the magnetic field. Therefore, the field dependent part of the spin fluctuations, which causes the significant enhancement of $1/T_1 T$ at low field, are dominated by $\chi(Q)$, where $Q$ is the AFM wave vector. Thus, the different field dependence between the Knight shift and $1/T_1 T$ suggests the coexistence of the spin fluctuations with $q = 0$ and $q = Q$.

Similar behavior is observed in NdRu$_4$P$_{12}$ and it suggests the coexistence of the spin fluctuations with $q = 0$ and $q \neq 0$[5]. They suggest that the dual magnetic correlations in NdRu$_4$P$_{12}$ is related with the Fermi-surface (FS) nesting property, which is common in $RRu_4P_{12}$ systems, and the nesting property competing with the FM correlation leads to much lower transition temperature for NdRu$_4$P$_{12}$. On the other hand, the recent experiments of de Haas-van Alphen effect have confirmed that no nesting property in the FS of $ROs_4P_{12}$ ($R = La, Pr, Nd$)[4, 6, 7], in contrast to good nesting properties in $RFe_4P_{12}$ and $RRu_4P_{12}$, which suggests that the origin of the strong field effect of $1/T_1 T$ in NdOs$_4P_{12}$ is different from that in NdRu$_4$P$_{12}$.

4. Conclusion

We have carried out electrical, magnetic and NMR experiments for filled skutterudite NdOs$_4P_{12}$ in order to elucidate the electronic states at low temperatures. NdOs$_4P_{12}$ shows metallic behavior in the electric resistivity and undergoes a ferromagnetic transition at 1.15 K. The Knight shift increases upon cooling and little depends on the magnetic field except for below 10 K. On the other hand, $1/T_1 T$ is largely enhanced with decreasing temperature and is strongly suppressed by the magnetic field, in contrast to the Knight shift. The different field dependence between the Knight shift and $1/T_1 T$ suggests the coexistence of the FM and AFM spin fluctuations.

Acknowledgments

We would like to express thanks to Prof. Y. Kitaoka and Prof. H. Mukuda for their help during the experiments at high magnetic fields. This work was supported by a Grants-in-Aid for Scientific Research (No.21540339) from the Japan Society for the Promotion of Science and the Ministry of Education, Culture, Sports, Science and Technology of Japan, and NSG Foundation.

References

[1] Torikachvili M.S, Chen J.W, Dalichaouch Y, Guertin R.P, McElfresh M.W, Rossel C, Maple M.B, Meisner G.P, 1987 Phys. Rev. B 36 8660
[2] Sato H, Abe Y, Okada H, Matsuda T.D, Abe K, Sugawara H and Aoki Y 2000 Phys. Rev. B 62 15125
[3] Sugawara H, Abe Y, Aoki Y, Sato H, Hedo M, Settai R, Onuki Y and Harima H, 2000 J. Phys. Soc. Jpn. 69 2938
[4] Iwahashi Y, Sugawara H, Magishi K, Saito T, Koyama K, Settai R, Onuki Y, Giester G and Rogl P, 2008 J. Phys. Soc. Jpn. 77 Suppl. A, 219
[5] Masaki S, Mito T, Wada S, Sugawara H, Kikuchi D and Sato H, 2008 Phys. Rev. B 78 094414
[6] Sugawara H, Iwahashi Y, Magishi K, Saito T, Koyama K, Harima H, Kikuchi D, Sato H, Endo T, Settai R, Onuki Y, Wada N, Kotegawa H and Kobayashi T.C, 2008 J. Phys. Soc. Jpn. 77 Suppl. A, 108
[7] Sugawara H, Iwahashi Y, Magishi K, Saito T, Koyama K, Harima H, Kikuchi D, Sato H, Endo T, Settai R and Onuki Y, 2009 Phys. Rev. B 79 035104