NMR studies on EuNi$_2$Si$_2$ with trivalent Eu ion

T Koyama$^1$, F Ueyama$^1$, T Maruyama$^1$, K Ueda$^1$, T Mito$^1$, A Mitsuda$^2$ and H Wada$^2$

$^1$Graduate School of Material Science, University of Hyogo, Kamigori, Hyogo 678-1297, Japan
$^2$Department of Physics, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
E-mail: t-koyama@sci.u-hyogo.ac.jp

Abstract. We have performed $^{29}$Si nuclear magnetic resonance experiment to investigate microscopic magnetic properties of EuNi$_2$Si$_2$ with trivalent Eu ion. The temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ can be explained by considering the two relaxation processes: conduction electrons and the thermally activated spins in the excited levels of $J$-multiplet. The temperature dependence of the Knight shift could roughly be reproduced with the spin-orbit coupling constant estimated from $1/T_1$.

1. Introduction

Magnetism in Europium (Eu) compounds differs substantially depending on the electronic configuration of Eu ion. According to Hund’s rule, the divalent Eu ions (4$f^7$) bear a large 4$f$ magnetic moment ($J=S=7/2$ and $L=0$) and its magnetic susceptibility $\chi$ obeys the Curie-Weiss law. On the other hand, the trivalent Eu ions (4$f^6$) is nonmagnetic ground state ($L = S = 3, J=0$). Here, $S(L)$ is the total spin (orbital) angular momentum and $J$ is the total angular momentum. One of the characteristics of trivalent Eu ion is the narrow energy separation between the first-excited $J$-multiplet $^7F_1$ and the ground-state $^7F_0$. In the Russell-Saunders coupling scheme, the energy difference between adjacent levels is determined by the spin-orbit coupling constant $\lambda$ and be expressed by

$$E_J - E_{J-1} = \lambda J.$$  \hspace{1cm} (1)

As a result, the energy separation between $^7F_0$ and the first excited level is of the same order as $k_BT$ for Eu$^{3+}$ and Sm$^{2+}$. Therefore, the magnetism of the $J$-multiplet level is expected to contributes to $\chi$ [1].

In most of the intermetallic Eu compounds, the Eu$^{2+}$ state rather than the Eu$^{3+}$ state tends to be stable. Then only a few intermetallic Eu-based compounds have been reported to be in the Eu$^{3+}$ state, such as EuPd$_3$ [2, 3], EuNi$_5$ [4], and EuCo$_2$Si$_2$ [5].

EuNi$_2$Si$_2$ crystallizes in the ThCr$_2$Si$_2$ tetragonal structure and is also categorized as the Eu$^{3+}$ system. The trivalent Eu ions are identified on the basis of the Eu $L_{III}$ x-ray-absorption spectroscopy and the Eu Mössbauer effect [6]. However, magnetic properties of EuNi$_2$Si$_2$ have not been reported. We performed the $^{29}$Si nuclear magnetic resonance (NMR) measurement to investigate microscopically the magnetic properties and discussed a contribution of $J$-multiplet levels to static and dynamical properties of EuNi$_2$Si$_2$. 

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
2. Experimental

A polycrystalline sample of EuNi$_2$Si$_2$ was prepared by melting mixture of a Eu ingot and NiSi alloys in a molar rate of Eu : NiSi=1.1 : 2 in an argon arc furnace to compensate the loss of Eu during melting. The x-ray diffraction pattern shows that the formation of tetragonal EuNi$_2$Si$_2$ with a trace of the secondary phase. The sample shows the upturn in $\chi$ at low temperatures, implying a possible inclusion of a material with magnetic Eu$^{2+}$. For the NMR experiments, the sample was crushed into powder. The NMR measurement was carried out using a phase-coherent spin-echo spectrometer at the temperature range of 1.5 - 240 K and a constant magnetic field of 6.01 T. The NMR spectra were taken by changing the frequency and recording the integrated spin-echo intensity. The nuclear-spin lattice relaxation rate $1/T_1$ was measured using the saturation recovery method. The nuclear magnetization recovery curves could be fitted at any temperature with a standard single exponential function expected for these $I=1/2$ nuclei.

3. Experimental results

Figure 1 shows the temperature dependence of the $^{29}$Si NMR spectra. With increasing temperature, the spectra shift to higher frequency and decreases in width. Figure 2 shows the temperature dependence of Knight shift $K(T)$ derived from the peak position of the spectra. $K(T)$ shows negative values and an increase with temperature, following the convex downward curvature above 50 K. This will be discussed in the next section.

Figure 3 shows the temperature dependence of $1/T_1$ measured at the peak of the $^{29}$Si NMR spectra. At low temperatures, $1/T_1$ increases proportional to temperature as is typical for nonmagnetic metals, where the relaxation process is dominated by the thermal excitations of conduction electrons at the Fermi level. With further warming, $1/T_1$ increases more rapid, suggesting the appearance of an additional relaxation channel.
4. Discussion

First we will discuss the contribution of the excited $J$-multiplet levels to $1/T_1$. We assume that the observed $1/T_1$ is decomposed into two contributions as

$$
\frac{1}{T_1} = \left( \frac{1}{T_1} \right)_c + \left( \frac{1}{T_1} \right)_{\text{exc}},
$$

where the first term in the right side is the contribution of conduction band which follows the Korringa law ($1/T_1 \propto T$). The second term is the thermally activated 4f spins in the excited states of $J$-multiplet. Because of the nonmagnetic ground state of $^7F_0$ and the narrow energy separation between $^7F_0$ and magnetic excited levels, the level with a certain value of $J$ is expected to contribute to the relaxation process. It was proposed that, for Van Vleck paramagnets, the contribution of the magnetic dipole fluctuation in magnetic crystalline electric field (CEF) excited states can be expressed by $[7, 8, 9]$

$$
\left( \frac{1}{T_1} \right)_{\text{exc}} \propto \sum_{\Gamma_i} |\langle \Gamma_i | J_z | \Gamma_i \rangle|^2 \exp(-E_{\Gamma_i}/k_BT)/Z,
$$

where $\Gamma_i$ is a CEF eigenstate, $E_{\Gamma_i}$ is the CEF splitting between $\Gamma_i$ and the nonmagnetic ground state, and $Z$ is the single ion partition function. We applied eqn.(3) to $J$-multiplet levels. Since CEF parameters for EuNi$_2$Si$_2$ have not been reported, we considered only the first excited level $^7F_1$. Moreover, for simplicity, we assumed the degeneracy of $^7F_1$ triplet which is actually lifted by CEF. Then eqn.(3) can be rewritten as

$$
\left( \frac{1}{T_1} \right)_{\text{exc}} \propto \frac{\exp(-E_{J=1}/k_BT)}{1 + 3 \exp(-E_{J=1}/k_BT)}.
$$

Using eqn.(2) and (4), we performed the least-squares fit to the experimental $1/T_1$ and then obtained $E_{J=1}(= \lambda) \approx 443$ K. This value is comparable to other Eu$^{3+}$ compounds, such as EuPd$_3$($\lambda \approx 480$ K) [3] and EuBO$_3$(\lambda=471 K) [10].

Next we discuss $K(T)$. In the Russell-Saunders coupling scheme, the temperature dependence of $\chi$ of Van Vleck paramagnets is known to be calculated when $S$, $L$, $J$, and $\lambda$ are given [1, 3, 10]. In order to deduce $K(T)$ for EuNi$_2$Si$_2$, we employed the simplified model: the same value of
the hyperfine coupling fields $H_{hf}$ from the Curie law term and temperature independent term of each $J$ level in $\chi$. Then we applied the commonly used relation of

$$K(T) = K_0 + \frac{H_{hf}}{N_A \mu_B} \chi,$$

where $K_0$, $N_A$, and $\mu_B$ are an on-site contribution of a conduction electrons, Avogadros number, and the Bohr magneton, respectively. Using eqn.(5), $K(T)$ above 100 K could be reproduced by the calculated $\chi$ with $H_{hf} \approx -0.81$ T/$\mu_B$ and $K_0=0.07\%$ as drawn by the red line in Fig.2. At low temperatures, $K(T)$ continues to decrease with temperature in contrast to the temperature independent behavior of the calculated data. As shown in the inset of Fig. 2, we observed that the full width at half maximum (FWHM) of $^{29}$Si NMR line divided by $|K(T)|$ showed an apparent increase below 100 K where $K(T)$ deviated from the calculation curve. These facts imply that $K(T)$ at low temperatures is affected by a certain amount of impurity including Eu$^{2+}$ which bears a large magnetic moment. The CEF determination and the discussion about $H_{hf}$ from each CEF level using the single crystal of EuNi$_2$Si$_2$ are challenges for the future.

5. Conclusion
We have performed $^{29}$Si NMR measurement on the intermetallic Van Vleck paramagnet EuNi$_2$Si$_2$. The divalent Eu ions exhibit the unusual magnetic properties which arise because of its closely spaced $J$-multiplet levels above the nonmagnetic ground level. We observed the rapid increase in $1/T_1$ above 100 K which is explained by the fluctuation of magnetic dipole in the first excited state populated mainly at high temperatures. Based on the Russell-Saunders coupling scheme, $K(T)$ could be roughly reproduced by the deduced value of $\lambda$ from $1/T_1$. Therefore, in the case of Eu$^{3+}$, higher $J$ levels contribute appreciably to both $1/T_1$ and $K(T)$.

Acknowledgments
This work was supported by JPSJ KAKENHI Grant Number 26800193.

References
[1] Van Vleck J H 1932 The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, Oxford) p.235
[2] Harris I R and Raynor G V 1965 J. Less-common Met. 9 263
[3] Takeuchi T, Nakamura A, Hedo M, Nakama T, and Onuki Y 2014 J. Phys. Soc. Jpn. 83 114001

Figure 3. Temperature dependence of $1/T_1$. The solid green line represents the contribution of conduction electrons. The dotted red line represents the result of fitting by considering the contributions of conduction electrons and the $^7F_1$ multiplet.
[4] Bauminger E R, Felner I, and Ofer S 1978 J. Magn. Magn. Mater. 7 317
[5] Seiro S, Kummer K, Vyalikh D, Caroça-Canales N, and Geibel C 2013 Phys. Status Solidi B 250 621
[6] Wortmann G, Nowik I, Perscheid B, Kaindl G, and Felner I 1991 Phys. Rev. B 43 5261
[7] Sugawara K 1977 J. Phys. Soc. Jpn. 42 1161
[8] Tanida H, Takagi S, Suzuki H S, Satoh I, and Komatsubara T 2006 J. Phys. Soc. Jpn. 75 074721
[9] Tokunaga Y, Sakai H, Kambe S, Sakai A, Nakatsuji S, Harima H 2013 Phys. Rev. B 88 085124
[10] Takikawa Y, Ebisu S, and Nagata S 2010 J. Phys. Chem. Solids 71 1592