La-NMR Study on a La Dilute System of PrPb$_3$

Y Tokunaga$^1$, H S Suzuki$^2$, H Sakai$^1$, H Chudo$^1$, S Kambe$^1$, H Yasuoka$^1$, Y Homma$^3$, D Aoki$^3$ and Y Shiokawa$^3$

$^1$ASRC, Japan Atomic Energy Agency, Tokai, Naka, Ibaraki 319-1195, Japan
$^2$National Institute for Materials Science, Tsukuba 305-0047, Japan
$^3$IMR Tohoku University, Narita Oarai Higashiibaraki Ibaraki 311-1313, Japan

E-mail: tokunaga.yo@jaea.go.jp

Abstract. We report the first $^{139}$La-NMR measurements on a La dilute system of PrPb$_3$. We have succeeded to detect $^{139}$La-NMR signal on a powder sample of Pr$_{0.97}$La$_{0.03}$Pb$_3$ and extracted the temperature dependence of the Knight shift $^{139}K(T)$ in a temperature range between 1.5 and 220 K. $^{139}K(T)$ has been found to maintain a linear relation with the bulk-susceptibility $\chi_{\text{bulk}}(T)$ in wide temperature range, except for a small deviation in the temperature region below 6 K. The slopes of the $^{139}K$ vs $\chi_{\text{bulk}}$ plots yield for the hyperfine coupling constants $A_{hf}$ the value 375 Oe/$\mu_B$. From the NMR results, we discuss the effect of the La substitutions on microscopic magnetic properties of PrPb$_3$.

1. Introduction

The intermetallic compound PrPb$_3$ crystallizes in a simple AuCu$_3$-type cubic structure (Fig. 1(a)) and exhibits an exotic antiferro-quadrupolar (AFQ) ordering at low temperatures below $T_Q=0.4$ K [1]. From inelastic neutron-scattering experiments, the cubic crystalline-electrical-field (CEF) energy levels for Pr$^{3+}(f^2)$ have been determined, giving for the ground state a non-Kramers $\Gamma_3$ doublet and for the first excited state a $\Gamma_4$ triplet with an energy splitting of 19 K [2]. The non-Kramers $\Gamma_3$ ground state has no magnetic dipolar moment, but has electric quadrupolar and magnetic octupolar moments, which dominate the low temperature properties of PrPb$_3$.

As for the AFQ structure below $T_Q$, Onimaru et al. have performed neutron diffraction measurements using a single crystal of PrPb$_3$ [3]. It was found that the quadrupolar moments are modulated sinusoidally below $T_Q$. In addition, the modulated AFQ structure has been suggested to persist as $T \to 0$ at low field. From the analogy with the magnetic Kondo systems, the authors have proposed that the local quadrupole moment is partly quenched at very low $T$ due to the quadrupolar Kondo effect. Meanwhile, Kawae et al. have investigated the effects of La substitution in PrPb$_3$ [4]. Both PrPb$_3$ and LaPb$_3$ are known to have the AuCu$_3$ cubic structure with lattice parameters $a = 4.867$ and 4.903 Å, respectively. The AFQ ordering has been found to collapse with only 2.5% dilution of the Pr ions with nonmagnetic La ions. On the other hand, for a wide range of La concentrations above 2.5%, the system has been suggested to exhibit random two-level behavior attributed to the quadrupolar moments [4]. In addition, recent specific heat and neutron diffraction experiments have revealed the existence of a field-induced ordered state in Pr$_{0.97}$La$_{0.03}$Pb$_3$ a temperatures below $\sim 0.4$ K [5, 6].
In this paper, we report the first $^{139}$La-NMR measurements on a system of dilute La-substituted PrPb$_3$. The temperature dependence of the $^{139}$La-NMR spectrum has been measured on a powder sample of Pr$_{0.97}$La$_{0.03}$Pb$_3$. We show that the Knight shift $^{139}K(T)$ exhibits a linear dependence on the bulk susceptibility $\chi^{\text{bulk}}$ over a wide temperature range, except for a small deviation in the temperature region below 6 K. From the NMR data, we discuss the effect of La substitution on the microscopic electronic properties of PrPb$_3$.

2. Experimental results

A powder sample of Pr$_{0.97}$La$_{0.03}$Pb$_3$ was prepared by grinding several small crystals grown by the Bridgeman method. The $^{139}$La NMR measurements were carried out using a superconducting magnet and a phase coherent, pulsed spectrometer. The temperature dependence of the NMR spectrum was measured by recording the integrated spin-echo intensity as a function of the applied magnetic field.

Figure 1(b) shows a series of field-sweep $^{139}$La-NMR spectra obtained at temperatures of 1.6, 10, 32, and 90 K, respectively. The NMR spectra broaden drastically with decreasing temperature, while they keep a symmetric line shape for the whole temperature range. The symmetric line shape indicates that there is no quadrupole splitting and no appreciable anisotropic NMR shift at the La sites, even though the $^{139}$La nucleus ($I = 7/2$) possess a nuclear quadrupole moment. The NMR spectra therefore provide microscopic evidence that cubic symmetry is preserved at the La sites. The temperature-dependent NMR line broadening may be attributed to a distribution of isotropic Knight shifts, which is associated in general with randomly varying contributions from nuclei having slightly different environments.

Figure 2 shows the temperature dependence of the Knight shift $^{139}K(T)$. $^{139}K(T)$ values were determined from the centers of gravity of the NMR lines. $^{139}K(T)$ is seen to increase rapidly with decreasing temperature. As we shall see below, the temperature dependence scales with that of the bulk susceptibility $\chi^{\text{bulk}}(T)$ over a wide temperature range. Note that the Knight shift values observed here are greatly enhanced relative to those in LaPb$_3$. Values of $^{139}K(T)$ reach $\sim 5\%$ at low temperatures in our sample, while those in LaPb$_3$ were reported to be $0.15\%$ at 300 K and $0.01\%$ at 4.2 K, respectively [7]. The large values of $^{139}K$ are attributed to transferred hyperfine (HF) fields from the Pr 4f electrons.
3. Discussion

Here we assume that $^{139}K(T)$ is dominated by the transferred HF fields from the six nearest-neighbor (n.n.) Pr ions surrounding a La ion, and hence $^{139}K(T)$ may be expressed as follows,

$$^{139}K(T) = 6 \frac{A_{hf}}{N_A \mu_B} \chi_{n.n.}^{Pr}(T),$$

where $^{139}A_{hf}$ is the transferred HF coupling constant between a $^{139}$La nuclear spin and a neighboring Pr 4f spin moment, $N_A$ is Avogadro’s number and $\mu_B$ is the Bohr magneton. $\chi_{n.n.}^{Pr}(T)$ represent the local spin susceptibility of the Pr sites. In Fig. 3, we plot $^{139}K$ vs $\chi_{bulk}$ with temperature as an implicit parameter. $^{139}K(T)$ maintains a linear dependence on $\chi_{bulk}(T)$ over a wide temperature range, except for a deviation in the temperature region below 6 K. From the linear dependence obtained here, we can confirm that the observed NMR signals come from grains of $\text{Pr}_{0.97}\text{La}_{0.03}\text{Pb}_3$, not from a minor impurity phase with La (if such a phase existed). Furthermore, the linear dependence suggests rather uniform magnetization in the sample, i.e., $\chi_{n.n.}^{Pr} \simeq \chi_{bulk}$ in Eq.(1). This indicates that the CEF level scheme does not change notably even at the n.n. Pr sites, i.e. the $\Gamma_3$ ground state is preserved. From the slopes of the $K$-$\chi$ plots, we evaluate the HF coupling constant $A_{hf} = 375 \text{ Oe}/\mu_B$ on the assumption of the $\chi_{n.n.}^{Pr} \simeq \chi_{bulk}$ at high temperatures.

On the other hand, $^{139}K(T)$ shows some deviation from linear dependence below 6 K. This anomaly might possibly be attributed to a small modification of the CEF level scheme around the La ions. However, we must remember that $\text{PrPb}_3$ is a Van Vleck paramagnet at low temperatures, where Pr nuclear spins strongly couple with electron spins through the HF interaction. Accordingly, the ordering of the Pr nuclear moments has been observed at the relatively high temperature of 5 mK [8]. Therefore, it is possible that the HF-enhanced nuclear magnetism makes an additional contribution to the Knight shift at low temperatures. Further experimental effort may be needed to clarify this point. Low-temperature NMR experiments, covering the field-induced ordered state, are currently in progress. The results will be reported elsewhere.
4. Summary

$^{139}$La NMR measurements have been performed on a powder sample of Pr$_{0.97}$La$_{0.03}$Pb$_3$. The linear relation between the Knight shift $^{139}K(T)$ and the bulk susceptibility $\chi(T)^{\text{bulk}}$ over a wide temperature range reveals that the CEF level scheme of the Pr ions does not change notably even around a La ion. The slope of the $^{139}K$ vs $\chi^{\text{bulk}}$ plot yields for the HF coupling constant $A_{hf}$ the value 375 Oe/$\mu_B$. On the other hand, $^{139}K(T)$ deviates from a linear relation to $\chi^{\text{bulk}}$ at temperatures below 6 K. As possible origins of this anomaly, we have proposed contributions from HF-enhanced Pr nuclear magnetism, as well as small modifications of the CEF level scheme for Pr sites neighboring the La dopant sites. The present NMR results demonstrate that microscopic investigations of La-diluted PrPb$_3$ is possible by means of $^{139}$La NMR.

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References

[1] E. Bucher, K. Andres, A. C. Gossard and J. P. Maita 1974 Proc. 13th Int. Conf. Low Temperature Physics vol 2 (New York: Plenum Publishing ) p 322.
[2] Gross W, Knorr K, Murani A P and Buschow H J 1980 Z. Phys. B 37 123.
[3] Onumaru T, Sakakibara T, Aso N, Yoshizawa H, Suzuki H S and Takeuchi T 2005 Phys. Rev. Lett. 94 197201.
[4] Kawae T, Shimogai M, Mito M and Takeda K 2001 Phys. Rev. B 65 012409.
[5] Nakaie Y, Akashi J, Hidaka M, Kawae T, Kitai T, Onimaru T and Suzuki H S 2006 Meeting abstract of the Physical Society of Japan, vol 61 issue 1 part 3 p 592.
[6] Onimaru T, Sakakibara T, Aso N, Sato T J, Yoshizawa H, Suzuki H S 2006 Meeting abstract of The Physical Society of Japan, vol 61 issue 2 Part 3 p 517.
[7] Welsh L B, Toxen A M and Gambino R J 1972 Phys. Rev. B 6 1677.
[8] Abe S, Takahashi D, Mizuno H, Ryu A, Asada S, Nahaer S, Matsumoto K, Suzuki H and Kitai T 2003 Physica B 329-333 637.