Anomalous behavior of the magnetic hyperfine field at ^{140}Ce impurities at La sites in $LaMnSi_2$

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Magnetic hyperfine field has been measured in the orthorhombic intermetallic compound $LaMnSi_2$ with perturbed angular correlation (PAC) spectroscopy using radioactive ^{140}La(^{140}Ce) nuclear probes. Magnetization measurements were also carried out in this compound with MPSM-SQUID magnetometer. Samples of $LaMnSi_2$ compound were prepared by arc melting the component metals with high purity under argon atmosphere followed by annealing at 1000°C for 60 h under helium atmosphere and quenching in water. X-ray analysis confirmed the samples to be in a single phase with correct crystal structure expected for $LaMnSi_2$ compound. The radioactive ^{140}La ($T_{1/2}$ = 40 h) nuclei were produced by direct irradiation of the sample with neutrons in the IEA-R1 nuclear research reactor at IPEN with a flux of ~ 10^{13} n $cm^{-2}s^{-1}$ for about 3 - 4 min. The PAC measurements were carried out with a six BaF_2 detector spectrometer at several temperatures between 10 K and 400 K. Temperature dependence of the hyperfine field, B_{hf} was found to be anomalous. A modified two-state model explained this anomalous behavior where the effective magnetic hyperfine field at ^{140}Ce is believed to have two contributions, one from the unstable localized spins at Ce impurities and another from the magnetic Mn atoms of the host. The competition of these two contributions explains the anomalous behavior observed for the temperature dependence of the magnetic hyperfine field at ^{140}Ce. The ferromagnetic transition temperature (T_C) of $LaMnSi_2$ was determined to be 400(1) K confirming the magnetic measurements. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5006897

I. INTRODUCTION

A series of intermetallic compounds $RMnSi_2$, where R is a rare earth element, crystallize in an orthorhombic $TbFeSi_2$-type structure belonging to space group (*Cmcm*). This structure can be described as built on alternating (010) planes containing R, Mn and Si atoms in a sequence Mn-Si-R-Si-Si-R-Si-Mn. Between each Mn-layer six nonmagnetic layers are sandwiched. This structure is closely related to the tetragonal $ThCr_2Si_2$-type structure of $RMn_2(Si, Ge)_2$ compounds which have been studied by different techniques.[1–5] The much less studied $RMnSi_2$ compounds have been investigated in the past by X-ray and neutron diffraction,[6] magnetization[7,8] and perturbed angular correlation (PAC) measurements using ^{111}Cd probe.[9] In these compounds, the Mn sub-lattice orders ferromagnetically up to high temperatures with T_C values well above room temperature. At lower temperatures additional magnetic transitions due to the ordering of rare earth atom sublattices appear in some case. $LaMnSi_2$ remains ferromagnetic even at low temperatures. The only magnetic atom in

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this compound is Mn which carries a local magnetic moment of 2.6 μB and the moments are aligned along stacking c-axis of the structure.[6] The ferromagnetic behavior of this compound is mainly due to long range Mn-Mn interactions. Despite some of the earlier studies on the structural and magnetic properties of $LaMnSi_2$ investigation of this compound using microscopic techniques are scarce. In this work we report on the results of temperature dependence of magnetic hyperfine field (B_{hf}) in $LaMnSi_2$ measured by Perturbed Angular Correlation (PAC) spectroscopy using ^{140}La(^{140}Ce) nuclear probe.

II. EXPERIMENTAL PROCEDURE

The sample of $LaMnSi_2$ was prepared by melting high purity elements (La = 99.9%, Mn = 99.99% and Si = 99.999%) in stoichiometric proportions in an arc furnace under argon atmosphere. After melting, the sample was sealed in a quartz tube under helium atmosphere and annealed for 60 hours at 1000^0C and then quenched in water. The radioactive nuclei, ^{140}La were produced by neutron irradiation of the sample in the IEA-R1 nuclear research reactor at IPEN. The irradiated sample was annealed at 1000^0C under helium atmosphere for 24 hours before starting the PAC measurement in order to minimize the effects of eventual radiation damage by fast neutrons during irradiation. PAC measurements were performed by using a six BaF_2 detectors spectrometer. The gamma cascade of 328-487 keV, with a 2084 keV intermediate state (magnetic moment μ = 4.35 (10) μ_N[10]) in ^{140}Ce populated from the beta decay of ^{140}La was used for the PAC measurements. Because the quadrupole moment ($Q \sim 0.35$ (7) b[11]) of the intermediate state is quite small, ^{140}Ce nucleus is mainly sensitive to the magnetic dipole interactions. Further details about PAC technique and the experimental method can be found in references 12 and 13. The PAC spectra were measured at different temperatures between 10 K and 400 K.

III. RESULTS AND DISCUSSION

The $LaMnSi_2$ samples were analyzed by powder X-ray diffraction and the spectra were refined with Rietveld method using Rietica software.[14] The orthorhombic crystal structure was confirmed for $LaMnSi_2$. The results of PAC measurements were analyzed with only magnetic dipole interactions for reasons pointed out earlier since the intermediate nuclear state at 2084 keV involved in the PAC measurement with ^{140}Ce probe has a very small quadrupole moment. The PAC spectra showed an unique and well defined magnetic interaction. Some of the PAC spectra for the compound $LaMnSi_2$ measured at different temperatures are shown in Fig. 1. It is quite obvious that the ^{140}Ce nuclear probe occupies the La atom site in $LaMnSi_2$ as this nucleus is produced from the β^--decay of ^{140}La formed in the sample through neutron irradiation. Temperature dependence of magnetic hyperfine field B_{hf} is shown in Fig. 2. It can be observed that the hyperfine field does not follow the normal Brillouin function for the host magnetization with spin 5/2 and its behaviour is anomalous. Field increases with decreasing temperatures up to about 200 K, decreases till 75 K and then increases again. The results further show that the hyperfine field seems to follow the Brillouin functions between 400 K and 200 K. The ferromagnetic transition temperature (T_C) of $LaMnSi_2$ was determined to be 402(1) K confirming the earlier results.[9] Results of magnetization measurements carried out with a magnetic property measurement systems superconducting quantum interference device (MPSM-SQUID) are shown in Fig. 3. The magnetization results are normal and do not show anomaly at lower temperatures observed in the hyperfine field.

Anomalous temperature dependence of hyperfine field measured with ^{140}La(^{140}Ce) nuclear probe in $LaMnSi_2$ contrasts with the results of the measurements of the same compound using ^{111}In(^{111}Cd) probe[9] where the hyperfine field follows the normal behaviour expected for the host magnetization with spin 5/2. In order to compare the two results it must be remembered that whereas in the present study the hyperfine field is measured at ^{140}Ce substituting La atom site, the measurement with ^{111}In(^{111}Cd) probe represent the field at ^{111}Cd substituting Mn atom sites. This is an important distinction, however it is also well known that the only magnetic atom in $LaMnSi_2$ is Mn which carries a local moment of 2.6 μ_B and these are aligned ferromagnetically along the stacking c-axis of

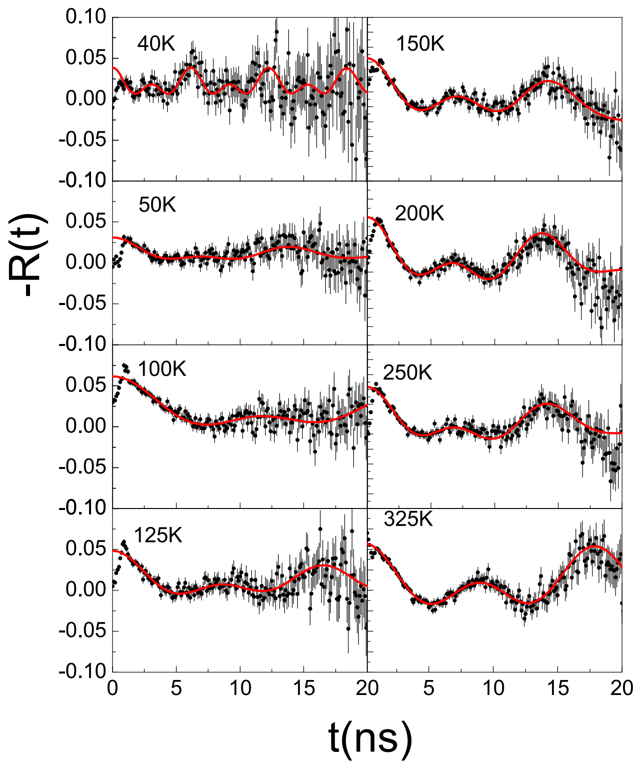

FIG. 1. Spin rotation functions R(t) for $LaMnSi_2$ with ^{140}Ce probe nuclei at several temperatures. Solid lines are the least squares fit of the theoretical functions to the experimental data.

the structure.[6] The ferromagnetic behavior of this compound is therefore mainly due to long range Mn-Mn interactions. The anomaly observed in the case of PAC measurements with ^{140}La(^{140}Ce) probe at low temperatures could therefore be attributed to some kind of interaction involving the probe atom Ce. Unlike ^{111}Cd where the probe atom is diamagnetic, the Ce atom in its normal trivalent state (Ce^{+3}) has one f-electron (f^1) which could interact with the magnetic field of the Mn sub-lattice. It is noteworthy that in $CeIn_3$, where the magnetic ions are Ce atoms, the temperature dependence of B_{hf} measured with ^{140}Ce follows the expected normal behavior.[15]

The first evidence of anomalous hyperfine field of very dilute Ce impurity in Gd was obtained by Thiel et.al.[16] in a PAC measurement with ^{140}La(^{140}Ce) probe. These authors ascribed this anomaly to the fluctuating valence state of Ce. Since then a large number of magnetic binary and ternary intermetallic compounds containing rare earth elements have been investigated using ^{140}La(^{140}Ce) probe.[17–20] In quite a few cases anomalous behavior of the hyperfine field has been observed at low temperatures. These anomalies have been attributed to the Ce 4f-electron contribution to B_{hf}. The phenomena is closely related to the fact that in Ce atom the energy of 4f level is quite close to the valence 5d and 6s levels and consequently only small energy changes are necessary to alter the relative occupancy of these electronic states. This fact makes the system with Ce impurity highly sensitive to the external effects such as temperature, pressure and fields. In $LaMnSi_2$ the anomaly of the temperature dependence of hyperfine field can be attributed to an interaction where f-electron of the probe Ce atom is spin polarized by the magnetic field from Mn sublattice and contributes to the effective hyperfine field. Below ferromagnetic transition temperature T_C = 400 K down till 200 K the observed hyperfine field at ^{140}Ce substituting La atoms is mainly due to long range magnetic interaction with local moment at Mn, such as RKKY interaction, and follows the normal Brillouin function. Between 200 K and 75 KB_{hf} decreases instead of continuing to increase to a saturation value. This decrease in B_{hf} is a consequence of the polarization of Ce-f-electrons by the Mn sub-lattice that results in f-electron spins aligning antiparallel[21] to the Mn spins in a gradual manner as a function of temperature and the effective field reduces from ~ 8.8 T at 200 K to ~ 1.4 T at ~ 75 K.

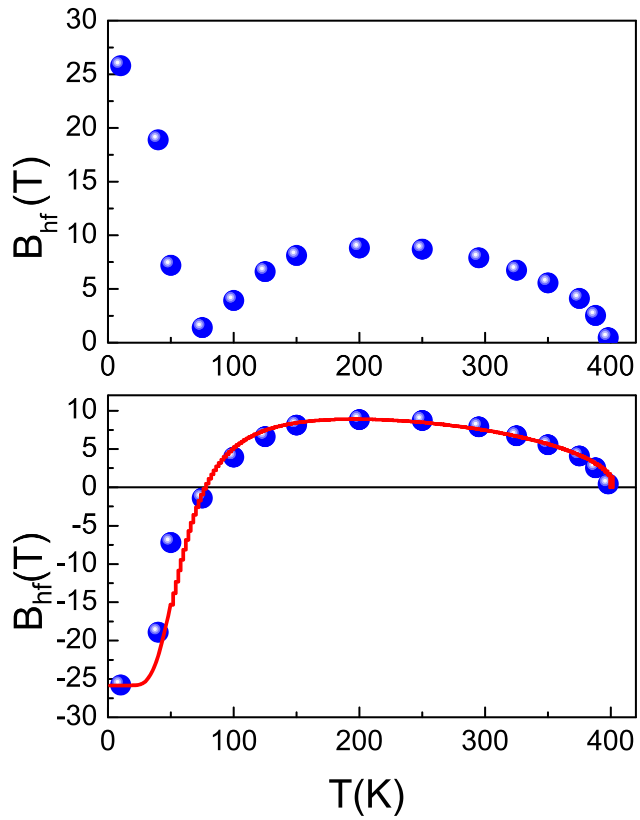

FIG. 2. Temperature dependence of the magnetic hyperfine field of ^{140}Ce in $LaMnSi_2$ (upper frame). Temperature dependence of the magnetic hyperfine field of ^{140}Ce in $LaMnSi_2$ re-plotted taking in to account its sign (lower frame). The solid line corresponds to the fit of the two-level model as explained in the text.

Below ~ 75 K till 10 K, the lowest temperature at which the measurements were made, the Ce-f-electron polarization is higher than the host (Mn) contribution resulting in an increase in the absolute value of B_{hf} with the decrease in the temperature.

We have measured the sign of B_{hf} by applying an external magnetic field of about 0.5 T normal to the plane of the four-detector spectrometer. In this method[22] using the configuration of 90^0 between

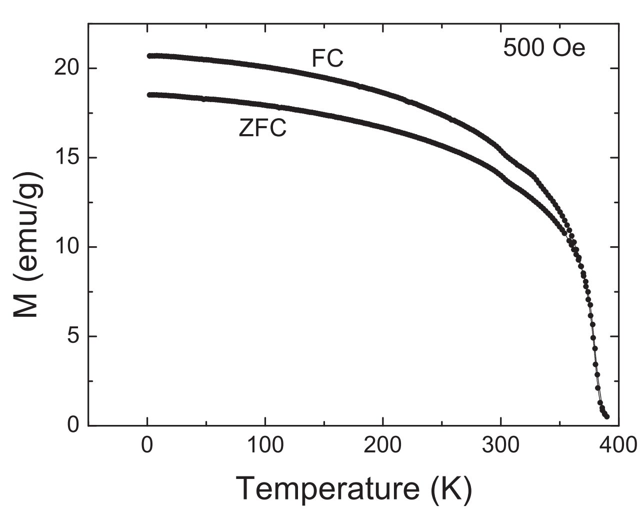

FIG. 3. Results for zero-field cooled (ZFC) and field cooled (FC) magnetization measurements with external field of 500 Oe.

detectors, one obtains a spin-rotation spectrum characterized by a frequency which is twice the Larmor frequency. If the Larmor frequency is larger as compared to the Larmor frequency measured without the external magnetic field, the Bhf should be positive, on the other had if the measured Larmor frequency is lower, the B_{hf} is negative.[22] We carried out measurements with an external magnetic field at 50 K, 75 K, 100 K, 200 K and 300 K. Results showed that the field is negative for 50 K and 75 K and positive for higher temperatures. For example, at 50 K the fields are 7.2 ± 0.1 T and 6.9 ± 0.3 T and at 200 K, 8.8 ± 0.1 T and 9.6 ± 0.3 T, without and with an external field, respectively. We then re-plot (see Fig. 2) the temperature dependence of B_{hf} taking into account its sign.

In order to analyze the contributions from *f*-electron of Ce and from Mn ions to B_{hf}, we adapted a model developed by Campbell[23] in which the Ce-*f*-electron is considered to be in two magnetic moment states: a high moment state with well-localized *f* band and a low moment state with a delocalized f band. In this two-state model, a magnetic hyperfine field at impurity nuclei (^{140}Ce) is associated to each state. These fields are B_{hf}^{host}, corresponding to the host contribution (low moment state) and B_{hf}^{Ce} related to the Ce ion contribution (high moment state) to the measured magnetic hyperfine field at ^{140}Ce, so that the total magnetic hyperfine field at ^{140}Ce on La sites is given by $B_{hf} = B_{hf}^{host} + B_{hf}^{Ce}$. This model was fitted to experimental data and the results are displayed in Fig. 2 as a solid line.

Results of the fit are B_{hf}^{host} = 12.4 T and B_{hf}^{Ce} = - 38.3 T. The magnetic hyperfine field at Mn sites in $LaMnSi_2$ was previously measured with ^{111}Cd probe and the result at the saturation region was B_{hf}^{Cd} = 7.0 T.[9] It is interesting to compare these results with those for $LaMn_2Si_2$.[3,19] The magnetic hyperfine field at ^{111}Cd on Mn sites in $LaMn_2Si_2$ at the saturation region was reported to be B_{hf}^{Cd} = 17.5 T[19] and the fit of the model to experimental results of B_{hf} for ^{140}Ce at La sites in $LaMn_2Si_2$ results in B_{hf}^{host} = 10.5 T and B_{hf}^{Ce} = 12.9 T. The higher value of B_{hf}^{host} at La sites in $LaMnSi_2$ when compared to that for $LaMn_2Si_2$ is a consequence of the shorter distance between La and Mn sites: d_{La-Mn} = 3.325 Å and d_{La-Mn} = 3.356 Å, respectively. However, the big difference in B_{hf}^{Cd} values cannot be ascribed only to the small difference in distances between intra-layer Mn sites (d_{Mn-Mn} = 2.92 Å and d_{Mn-Mn} = 2.909 Å for $LaMnSi_2$ and $LaMn_2Si_2$, respectively). This difference is due to the inter-layer Mn-Mn distances which is much higher for $LaMnSi_2$ (d_{Mn-Mn} = 8.89 Å) than for $LaMn_2Si_2$ (d_{Mn-Mn} = 5.30 Å).

The most intriguing results are those for B_{hf}^{Ce}, which are quite different for $LaMnSi_2$ and $LaMn_2Si_2$. Moreover, the temperature dependence of B_{hf} for the later does not present an anomalous behavior despite the polarization of *f*-electrons of Ce.[24] To understand these observations we must consider the results of the fit of the two-level model for the difference in the 0 K energy (E_0) between the low and high moment states (E_0 = 25 meV for $LaMnSi_2$ and E_0 = 53 meV for $LaMn_2Si_2$). E_0 is related to the exchange interaction energy between 3*d* electrons of Mn and 4*f* electrons of Ce and it is directly proportional to the intensity of the exchange interaction. Therefore, higher the E_0 value stronger is the exchange interaction. The lower Ce contribution intensity for $LaMn_2Si_2$ (B_{hf}^{Ce} = 12.9 T) along with a stronger exchange interaction make the 4*f* spins of Ce impurities follow closely the magnetization of Mn ions resulting in a Brillouin-like behavior for the temperature dependence of B_{hf}. Conversely, a higher absolute intensity of Ce contribution for $LaMnSi_2$ (B_{hf}^{Ce} = - 38.3 T) and a weaker exchange interaction leave the 4*f*-spins of Ce, despite being polarized by the magnetic field of the host, in a loosely antiferromagnetic coupling with the 3*d* electrons of Mn which presents a departure from a Brillouin-like behavior for B_{hf} as a function of temperature.

IV. SUMMARY

Results for B_{hf} x temperature in $LaMnSi_2$ indicate that, in the temperature range from 400 K to 200 K, a long range interaction of RKKY type due to ferromagnetic sub-lattice of Mn atoms is believed to be the mechanism responsible for the observed hyperfine field at ^{140}Ce substituting La. Strong deviation from the normal Brillouin type behavior at lower temperatures is believed to be due to polarization of Ce-*f* electrons by the field from ferromagnetic sub-lattice of Mn atoms. In order to analyze the contributions from *f*-electron of Ce and from Mn ions to B_{hf}, a two-state model was used. This two-state model explains very well the observed anomalous temperature dependence of hyperfine field at ^{140}Ce probe nuclei in $LaMnSi_2$.

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