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Effect of Ge substitution for Si on the magnetic hyperfine field in $LaMn_2Si_2$ compound measured by perturbed angular correlation spectroscopy with ^{140}Ce as probe nuclei

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The effect of substitution of Ge for Si in $LaMn_2Si_2$ compound on the magnetic hyperfine field (B_{hf}) has been investigated by perturbed $\gamma-\gamma$ angular correlation (PAC) spectroscopy using $^{140}La(^{140}Ce)$ as probe nuclei. This compound exhibits antiferromagnetism followed by a ferromagnetic ordering when temperature decreases. The behavior of the ferromagnetic transition when Ge gradually replaces Si, with concentrations of 20%, 40%, 80%, and 100% is discussed. PAC measurements were carried out in the temperature range from 15 K to 325 K. Results for $LaMn_2Si_2$ compound showed that the dependence of B_{hf} with temperature follows the expected behavior for the host magnetization and could be fitted by a Brillouin function for $J_{Mn}=5/2$. However, the temperature dependence of B_{hf} for compounds when Si is gradually replaced by Ge showed a deviation from such a behavior, which gradually increases up to a strong deviation observed for $LaMn_2Ge_2$. This striking behavior was ascribed to the hybridization of *d* band of the host and *f* band of the Ce impurities, which is stronger when the unit cell volume increase as Si ions are substituted by Ge atoms. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795419]

I. INTRODUCTION

The RMn_2X_2 compounds, where *R* is a rare-earth element and $X=$ Si and Ge are *s-p* elements, crystallize in the $ThCr_2Si_2$ prototype structure which belongs to the *I*4/*mmm* space group. These compounds have been intensively studied in the last decades due to the large variety of interesting effects associated to them, such as a different magnetic ground-state structures, giant Magnetoresistance (GMR) properties, and metamagnetic transition.[1,2] Studies in this family of compounds have been focused in the mechanism of magnetic interaction between Mn-Mn and R-Mn, which can be distinguished in three different types of exchange interaction: (a) inter-layer exchange interaction Mn-Mn, (b) exchange interaction between the R and Mn sublattices, and (c) intra sublattice R-R exchange.[3] $LaMn_2X_2$ ($X=$ Si, Ge) compounds have been reported to undergo an antiferromagnetic followed by a ferromagnetic transition, when temperature decreases. Measurements of Möussbauer spectroscopy using ^{57}Fe with probe nuclei at the Mn atomic positions reported that antiferromagnetism to ferromagnetism transition occurs due to a strong spin reorientation relative to the crystalline axes.[4] However, the transition temperature between antiferromagnetic to ferromagnetic ordering, i.e., the Curie temperature (T_C) is not well characterized yet. For instance, it reported a range of 303–310 K for $LaMn_2Si_2$ and a range of 306–326 K for $LaMn_2Ge_2$.[5]

In this work, we have measured the temperature dependence of the magnetic hyperfine field (B_{hf}) in $LaMn_2(Si_{(1-x)}Ge_x)_2$ compounds by perturbed gamma-gamma angular correlation (PAC) spectroscopy using $^{140}La(^{140}Ce)$ as probe nucleus substituting La position in the crystal lattice. The great advantage of using this probe nucleus is that, due to its low electric quadrupole moment, only dipole magnetic interactions are observed, and as a consequence, B_{hf} can be determined with high precision without the interference of the electric quadrupole interactions. Moreover, due to the arrangement of Mn atoms in the crystal structure, in the antiferromagnetic phase, B_{hf} vanishes at La position as a consequence of the "spin up" and "spin down" symmetry of Mn atoms around the La sites. It was, therefore, possible to determine accurately the transition temperature of the ferromagnetic phase in the studied compounds.

II. EXPERIMENTAL PROCEDURE

The $LaMn_2(Si_{(1-x)}Ge_x)_2$, where $x=0$, 0.2, 0.4, 0.8, and 1, compounds were prepared by arc-melting the constituent elements (with purities of 99.9%, 99.999%, and 99.9999%, respectively, for La, Mn, and Si/Ge) in stoichiometric proportions, with approximately 20 wt. % excess of Mn, followed by annealing at 800 °C in low air pressure ($\sim 10^{-6}$ mbar) during 24 h. Samples were characterized by x-ray diffraction (XRD), whose results were analyzed by the Rietveld method with the RIETICA software.[7] XRD results showed only a single phase for all samples corresponding to the expected tetragonal structure of $ThCr_2Si_2$-type, which belongs to the I4/*mmm* space group.

Once the crystalline structure of samples had been determined to be in the correct phase, a part corresponding to approximately 15 mg of each sample was sealed in an evacuated quartz tube and irradiated with neutrons in the IEA-R1 research reactor of IPEN for 4 min followed by thermal treatment at 800 °C for 12 h. Natural La present in samples contains the ^{139}La isotope, which when irradiated with neutrons

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produces the ^{140}La radioisotope, the parent radioactive isotope of ^{140}Ce used for PAC measurements. The other constituent elements of the samples are not activated (Si) or have very short half-lives (Mn and Ge). Once the probe nucleus is produced by a nuclear transmutation of the ^{139}La isotope, which is one of the constituent elements of the compounds, the location of the ^{140}Ce probe nuclei used in PAC measurements is unambiguously determined. This procedure is another great advantage of using ^{140}La(^{140}Ce) as probe nuclei to investigate the magnetism in the studied compounds.

The PAC spectroscopy is based on the observation of hyperfine interactions of nuclear moments with extra-nuclear magnetic fields (B_{hf}) or with an electric field gradient. A description of the method as well as details about the PAC measurements can be found elsewhere.[8,9] PAC measurements were performed in a gamma spectrometer with six conical BaF_2 scintillator detectors in a conventional fast-slow coincidence setup. The measurements were carried out in the temperature range of 15 K to 325 K using a closed cycle helium cryogenic device.

The spin rotation spectra obtained in the measurements were fitted by using a model that takes into account the fractional site populations (f), which is given by

$$A_{22}G_{22}(t) = A_{22}\sum_i f_i G^i_{22}(t), \quad (1)$$

where A_{22} is the unperturbed angular correlation coefficient and the perturbation factor $G_{22}(t)$ contains detailed information about the hyperfine interaction. Experimental measurement of $G_{22}(t)$ allows, in the dipole magnetic interaction, the determination of the Larmor frequency $\omega_L = \mu_N g B_{hf}/\hbar$, where μ_N is nuclear magneton. Consequently, from the known g-factor ($g = 1.014$ (Ref. 10)) of the 487 keV intermediate state ($t_{1/2} = 3.4$ ns (Ref. 10)) of ^{140}Ce, the magnetic hyperfine field B_{hf} can be determined.

III. RESULTS AND DISCUSSION

Some PAC spectra for the studied compounds are shown in Fig. 1. It can be observed that few experimental points close to time equal to zero were not considered in the fit because they are affected by a strong prompt peak in the coincidence spectra.[11]

As expected, the measured PAC spectra showed the presence of a single fraction site with only magnetic frequency (ν_M). A Brillouin function with $J_{Mn} = 5/2$ fitted very well the behavior of the temperature dependence of B_{hf} for $LaMn_2Si_2$. However, as Si is gradually replaced by Ge, the temperature dependence of B_{hf} showed a deviation from such behavior, which gradually increases up to a strong deviation observed for $LaMn_2Ge_2$. For instance, this deviation can be observed in Fig. 2(a) for $LaMn_2(Si_{0.8}Ge_{0.2})_2$ compound. A similar anomalous behavior was previously observed[6] in measurement of the temperature dependence of B_{hf} measured with ^{140}Ce in $CeMn_2Ge_2$. This observed phenomenon was explained as an additional contribution to the B_{hf} due to polarization of the Ce spins moments induced by the magnetic field from Mn moments.[6] Recently, a similar

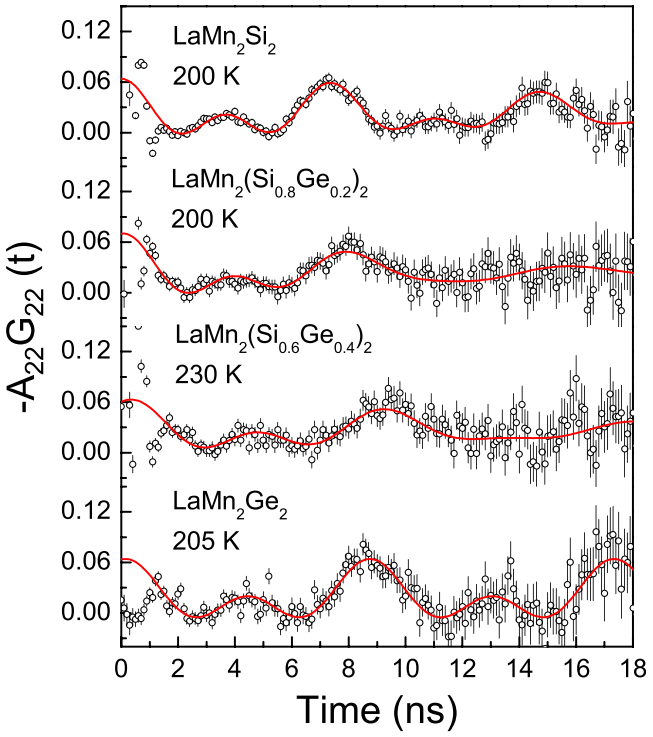

FIG. 1. The perturbation functions ($-A_{22}G_{22}$ (t)) for ^{140}Ce probe nuclei in $LaMn_2(Si_{(1-x)}Ge_x)_2$. The solid lines are the least square fit to the theoretical function.

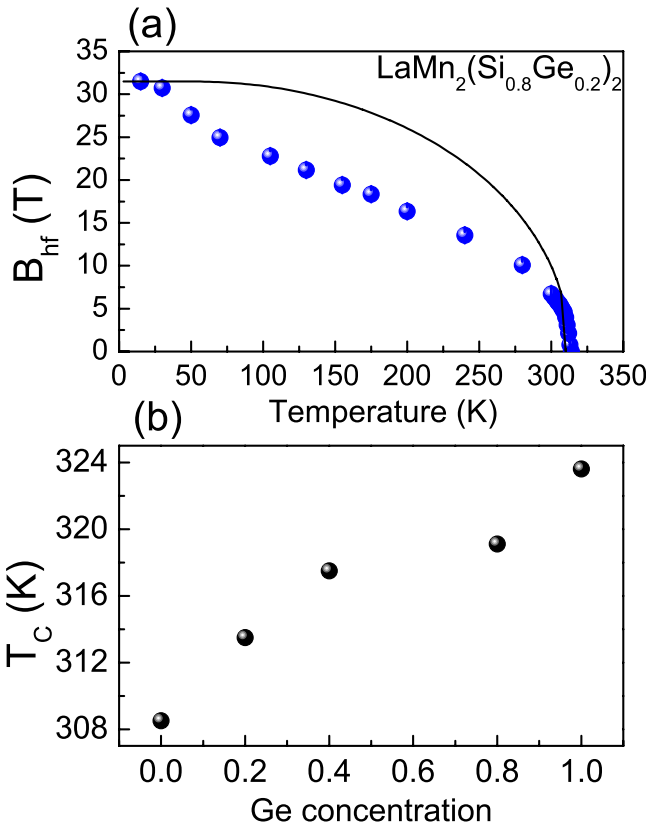

FIG. 2. (a) Temperature dependence B_{hf} at La sites measured with ^{140}Ce in $LaMn_2(Si_{0.8}Ge_{0.2})_2$. The solid line represents the Brillouin curve for $J_{Mn} = 5/2$. (b) Variation of the T_C with Ge concentration x for $LaMn_2(Si_{(1-x)}Ge_x)_2$.

TABLE I. Magnetic hyperfine field (B_{hf}), Curie temperature (T_C), critical exponent (β), and Mn-Mn distance (d_{Mn-Mn}) for the studied compounds. T_C and β were obtained from the fit of the critical exponent function (see text). d_{Mn-Mn} values were extracted from XRD results.

Compounds	B_{hf}[a] (T)	T_C (K)	β	d_{Mn-Mn} (Å)
$LaMn_2Si_2$	23.4 (6)	308.5 (2)	0.384 (1)	2.909 (1)
$LaMn_2(Si_{0.8}Ge_{0.2})_2$	31.5 (8)	313.1 (2)	0.406 (1)	2.919 (1)
$LaMn_2(Si_{0.6}Ge_{0.4})_2$	37.8 (9)	317.5 (2)	0.408 (1)	2.931 (1)
$LaMn_2(Si_{0.2}Ge_{0.8})_2$	40.8 (9)	319.1 (2)	0.400 (1)	2.953 (1)
$LaMn_2Ge_2$	43.3 (1.0)	323.3 (2)	0.410 (1)	2.965 (1)

[a]Value of the magnetic hyperfine field at 15 K.

deviation was also observed in $GdRh_2X_2$ (X = Si, Ge) compounds where Gd is the magnetic ion.[9] The anomalous behavior of the temperature dependence of B_{hf} was associates to Ce 4 *f* band, which is localized just below the Fermi level and hybridized with the host *d* band of Gd which is also localized near the Fermi level resulting in a delocalization of part of the Ce 4 *f* band, which can explain this anomalous behavior.[12] In $LaMn_2(Si_{(1-x)}Ge_x)_2$, with $x > 0$, probably the hybridization of Ce 4 *f* band with the *d* band of the Mn is also responsible for the anomalous behavior in these compounds.

The temperature dependence of the hyperfine field near the transition temperature was investigated by the fit of a model given by $B_{hf}(T) = B(0)(1 - T/T_C)^{\beta}$, where β is the critical exponent and $B(0)$ is B_{hf} at $T = 0$, to around 15 experimental points immediately below T_C. The resulting values for β are shown in the Table I for all samples. The exponent β was found to be almost the same for all compounds leading us to conclude that the ferromagnetic ordering is similar in all compounds. From the fit, values of T_C could be precisely determined, and the results are also displayed in Table I. Fig. 2(b) shows the dependence of T_C with the Ge concentration (x) and one can observe that the T_C increases when the Ge concentration increases. This effect is due the distance Mn-Mn (shown in the last column of Table I) which also increases when Ge concentration increases. As the crystalline structure and the magnetic ions are the same for all these compounds, the increase in Mn-Mn distance would result in a decrease in T_C. However, T_C is also directly proportional to the exchange constant J_{ex}, which is strongly dependent of the distance between the neighboring magnetic ions. We, therefore, conclude that J_{ex} strongly increases when Ge concentration increases, being, consequently, the predominant parameter for the magnetic behavior of the studied compounds.

IV. SUMMARY

PAC measurements of B_{hf} at ^{140}Ce probe nuclei in $LaMn_2(Si_{(1-x)}Ge_x)_2$ compounds were used to precisely determine the ferromagnetic ordering temperature in $LaMn_2Si_2$ and $LaMn_2Ge_2$ compounds as well as to investigate the behavior of T_C when the concentration of Ge increases. Results showed that the temperature dependence of B_{hf} for $LaMn_2Si_2$ could be fitted by a Brillouin function for $J_{Mn} = 5/2$, while the temperature dependence of B_{hf} for compounds when Si is gradually replaced by Ge showed a deviation from such behavior, which gradually increases up to a strong deviation observed for $LaMn_2Ge_2$. This behavior as well as the behavior of T_C was associated to the increase in the Mn-Mn distance when Si is substituted for Ge.

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