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## Magnetic behavior of $\text{LaMn}_2(\text{Si}_{(1-x)}\text{Ge}_x)_2$ compounds characterized by magnetic hyperfine field measurements

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The temperature dependence of the magnetic hyperfine field ( $B_{hf}$ ) at Mn atom sites was measured in  $\text{LaMn}_2(\text{Si}_{(1-x)}\text{Ge}_x)_2$ , with  $0 \leq x \leq 1$ , compounds with perturbed  $\gamma - \gamma$  angular correlation spectroscopy using  $^{111}\text{In}$  ( $^{111}\text{Cd}$ ) as probe nuclei in the temperature range from 20 K to 480 K. The results show a transition from antiferromagnetic to ferromagnetic ordering for all studied compounds when Ge gradually replaces Si and allowed an accurate determination of the Néel temperature ( $T_N$ ) for each compound. It was observed that  $T_N$  decreases when Ge concentration increases. Conversely, the Curie temperature increases with increase of Ge concentration. This remarkable change in the behavior of the transition temperatures is discussed in terms of the Mn-Mn distance and ascribed to a change in the exchange constant  $J_{ex}$ . © 2014 AIP Publishing LLC.  
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### I. INTRODUCTION

The compounds  $\text{LaMn}_2\text{Ge}_2$  and  $\text{LaMn}_2\text{Si}_2$ , which crystallize in the  $\text{ThCr}_2\text{Si}_2$ -type tetragonal structure belonging to the  $I4/mmm$  space group,<sup>1</sup> are known to exhibit strong antiferromagnetic behavior with a transition to ferromagnetic ordering near room temperature.<sup>2</sup> Moreover,  $\text{LaMn}_2\text{Ge}_2$  compound was found to exhibit a large positive magnetoresistance at low temperatures and, when doped with Fe, also presents a small magnetocaloric effect.<sup>3,4</sup> Mn ion in these compounds is the transition metal that possesses magnetic moment. The mechanism of magnetic interactions between Mn-Mn in this family of compounds has been investigated in terms of exchange interactions.<sup>5</sup> The exchange interactions can be mediated by two different modes: (1) The indirect exchange that occurs between two Mn planes through the conduction electron polarization process and (2) the super exchange mediated through the Mn-Si(Ge)-Si(Ge)-Mn chain.<sup>6</sup> To characterize the antiferromagnetic ordering with accuracy,  $^{57}\text{Fe}$  Mossbauer study was carried out and showed that the Mn sublattice probably is antiferromagnetically ordered up to 470 K and 415 K, respectively, for  $\text{LaMn}_2\text{Si}_2$  and  $\text{LaMn}_2\text{Ge}_2$ .<sup>2</sup> In the present work, the magnetic behavior of these compounds, when Si is gradually replaced by Ge, was investigated by measuring the magnetic hyperfine field ( $B_{hf}$ ) at Mn sites with perturbed  $\gamma - \gamma$  angular correlation (PAC) spectroscopy using  $^{111}\text{In}$  ( $^{111}\text{Cd}$ ) as probe nuclei. The behavior of  $B_{hf}$  and the variation of Néel temperature, when Ge substitutes Si, has been studied by determining the temperature dependence of the magnetic hyperfine field in  $\text{LaMn}_2(\text{Si}_{(1-x)}\text{Ge}_x)_2$  compounds ( $0 \leq x \leq 1$ ). PAC measurements using this particular probe nucleus are important in this compounds because the major fraction of  $^{111}\text{Cd}$  probes are found to substitute Mn sites in the crystal lattice, and, consequently, such measurements help in determining the arrangement of the Mn atoms in both the antiferromagnetic

and ferromagnetic phases as well as make it possible to determine the Néel temperature ( $T_N$ ) as the  $B_{hf}$  at Mn position vanishes.

### II. EXPERIMENTAL PROCEDURE

The samples of  $\text{LaMn}_2(\text{Si}_{(1-x)}\text{Ge}_x)_2$  were prepared by mixing the stoichiometric proportions of La (99.9% purity), Ge (99.999% purity), Si (99.999% purity), and Mn (99.999% purity). A little excess of Mn (around 5% by weight) was used to compensate the weight loss by evaporation. The mixed metals were arc-melted in a water cooled copper crucible under high purity argon atmosphere. After melting, the alloy was annealed in vacuum at 800 °C during 24 h. The structure and purity of the samples were determined by the room temperature powder x-ray diffraction (XRD) method, and the resulting XRD spectra were analysed by the Rietveld method. The fits for all samples confirmed a single phase corresponding to the  $\text{ThCr}_2\text{Si}_2$  structure with  $I4/mmm$  space group. After structural characterization, a small part of each sample was cut out. Approximately 20–30  $\mu\text{Ci}$  of carrier-free  $^{111}\text{In}$  solution (in the form  $^{111}\text{InCl}_3$  aqueous solution) was deposited on this slice of the sample, which was subsequently dried and alloy re-melted in the arc furnace. The resulting ingot in the form of a small sphere was sealed in an evacuated quartz tube and annealed at 900 °C for 20 h.

The PAC spectroscopy is based on the emission of two gamma radiations in a cascade as a result of nuclear decay of the excited state of the probe nucleus. The technique relies on the measurement of  $\gamma - \gamma$  angular correlation which is perturbed by the interaction between the nuclear moment (magnetic dipole moment and or electric quadrupole moment) of the intermediate nuclear state and extra nuclear fields (magnetic field or electric field gradient). The well-known gamma cascade of 172–245 keV in  $^{111}\text{Cd}$  was used to investigate the hyperfine interactions. Some of the measurements were performed using a PAC spectrometer with six conical  $\text{BaF}_2$  detectors while others were measured using the PAC

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spectrometer with four BaF<sub>2</sub> detectors, both associated with conventional fast-slow electronic setup to measure the delayed gamma-gamma coincidences. Measurements were carried out in the temperature range 20–480 K using a closed loop helium cryogenic system. Description of the method as well as details about the PAC measurements can be found elsewhere.<sup>7,8</sup> The results of the coincidence spectra were processed by a home developed software to obtain the perturbation function  $A_{22}G_{22}(t)$ . The function  $G_{22}(t)$  contains detailed information about the hyperfine interaction and can be modelled in terms of the magnetic dipole and or the electric quadrupole frequencies and allows the determination of the magnetic hyperfine field ( $B_{hf}$ ) and electric field gradient.

### III. RESULTS AND DISCUSSION

The PAC spectra for all compounds measured at room temperature are shown in Fig. 1. Solid lines in the spectra are the least square fit of an appropriate theoretical perturbation function to the experimental data. Below  $T_N$ , PAC spectra for all samples were characterized by two sites occupied by the probe nuclei. The major fraction (~75%) showed pure magnetic dipole interaction with well-defined Larmor frequency which vary with temperature. The minor fraction presents only electric quadrupole interaction with broadly distributed quadrupole frequencies. This is probably due to the probe nuclei at non substitutional sites. In the spectra at room temperature, one can observe a better diffusion of the radionuclide in LaMn<sub>2</sub>Ge<sub>2</sub> compound than the other

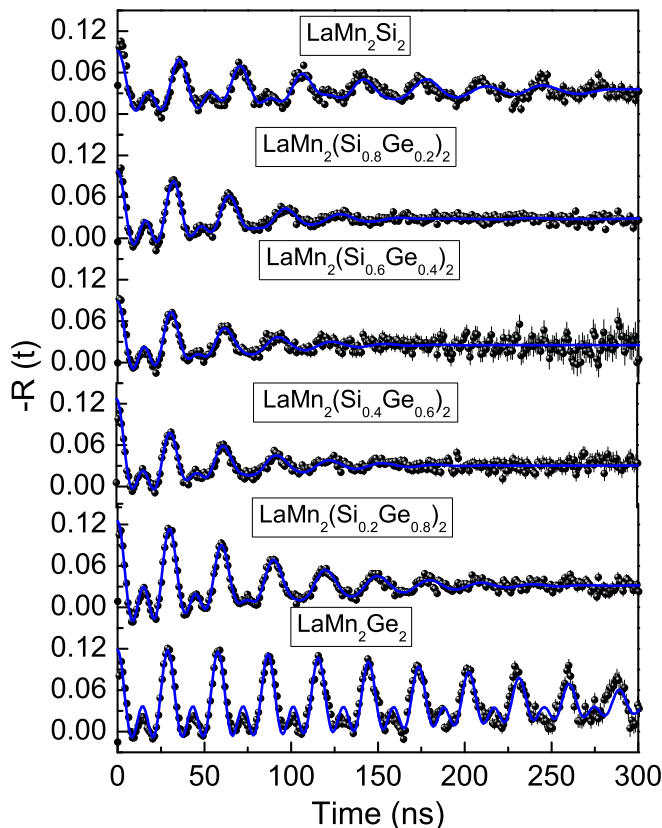


FIG. 1. Perturbation functions for <sup>111</sup>Cd probe in LaMn<sub>2</sub>(Si<sub>1-x</sub>)Ge<sub>x</sub><sub>2</sub> measured at room temperature. The solid lines are the least square fit to the theoretical function.

compounds because the crystal lattice LaMn<sub>2</sub>Ge<sub>2</sub> is bigger than LaMn<sub>2</sub>Si<sub>2</sub>. In the mixed compounds, there may be a small disorder in the crystal lattice as these contain many elements.

It is assumed that <sup>111</sup>Cd probe nuclei replace the Mn atoms in the observed major fraction. This assumption is based on the consideration of higher chemical affinity of <sup>111</sup>In for Mn rather than for La, Si, or Ge atoms and also based on previous results reported by Carbonari *et al.*<sup>9</sup> who performed PAC measurements in CeMn<sub>2</sub>Si<sub>2</sub> and CeMn<sub>2</sub>Ge<sub>2</sub> compounds using the same probe nuclei. Their experimental observations and *ab initio* calculations are quite consistent with the assumption that <sup>111</sup>Cd probes replace Mn atoms.<sup>9</sup>

The temperature dependence of  $B_{hf}$  measured with <sup>111</sup>Cd for LaMn<sub>2</sub>(Si<sub>1-x</sub>)Ge<sub>x</sub><sub>2</sub> ( $0 \leq x \leq 1$ ) is shown in Fig. 2 where the transition from an antiferromagnetic to ferromagnetic phase is clearly observed for all compounds in the temperature range from 306 K to 324 K. As the <sup>111</sup>Cd probe nucleus is nonmagnetic it only observes magnetic interactions from the neighbouring Mn atoms, and the observation of antiferromagnetic interactions is the strongest indication that <sup>111</sup>Cd probes replace Mn ions in the crystal lattice, inasmuch as if they were in La or Si/Ge sites the antiferromagnetic interaction would not be observed. The solid lines in Fig. 2 represent the fit of a Brillouin function with  $J_{Mn} = 3/2$  to the antiferromagnetic region of  $B_{hf}$  vs.  $T$  plots. From this fit, it was possible to determine  $T_N$  of each compound with

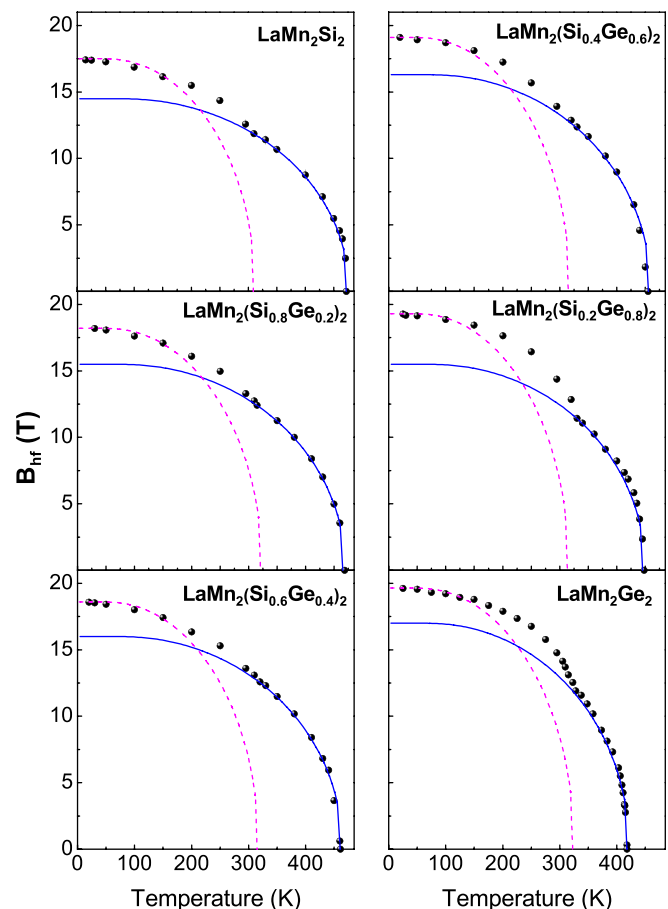


FIG. 2. Temperature dependence of  $B_{hf}$  at Mn sites occupied by <sup>111</sup>Cd probe nuclei in LaMn<sub>2</sub>(Si<sub>1-x</sub>)Ge<sub>x</sub><sub>2</sub> ( $0 \leq x \leq 1$ ).

TABLE I. Magnetic hyperfine field ( $B_{hf}$ ), Néel temperature  $T_N$ , Curie temperature ( $T_C$ ), Mn-Mn distance ( $d_{Mn-Mn}$ ), and Mn-X-Mn angle ( $X = \text{Si, Ge}$ ) for the studied compounds.

| Compounds   | $B_{hf}^a$ (T) | $T_N$ (K) | $T_C^b$ | $d_{Mn-Mn}$ (Å) | Mn-X-Mn angle (deg) |
|---|----------------|-----------|---------|-----------------|---------------------|
| $\text{LaMn}_2\text{Si}_2$                        | 17.5           | 470.0     | 308.5   | 2.909           | 111.87              |
| $\text{LaMn}_2(\text{Si}_{0.8}\text{Ge}_{0.2})_2$ | 18.2           | 465.6     | 313.1   | 2.919           | 112.12              |
| $\text{LaMn}_2(\text{Si}_{0.6}\text{Ge}_{0.4})_2$ | 18.6           | 460.2     | 315.6   | 2.931           | 111.99              |
| $\text{LaMn}_2(\text{Si}_{0.4}\text{Ge}_{0.6})_2$ | 19.1           | 455.0     | 317.5   | 2.943           | 111.84              |
| $\text{LaMn}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ | 19.3           | 444.5     | 319.1   | 2.953           | 111.66              |
| $\text{LaMn}_2\text{Ge}_2$                        | 19.6           | 418.0     | 323.3   | 2.965           | 111.33              |

<sup>a</sup>Value of the magnetic hyperfine field was extrapolate to 0 K.

<sup>b</sup>From Bosch-Santos in Ref. 10.

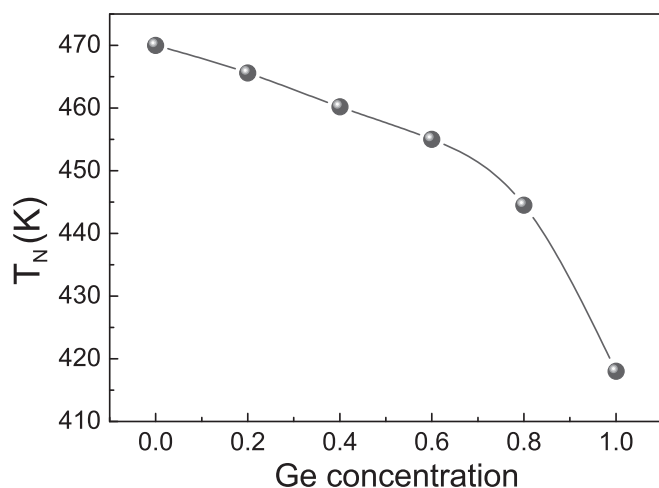


FIG. 3. Néel temperature as a function of Ge concentration in  $\text{LaMn}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ . The solid line is to guide the eyes.

accuracy. The results for  $T_N$  are presented in Table I along with the Curie temperature ( $T_C$ ) determined in a previous work,<sup>10</sup> except for  $\text{LaMn}_2(\text{Si}_{0.4}\text{Ge}_{0.6})_2$ , for which  $T_C$  is the estimated value from the present work. The fit of Brillouin function with  $J_{Mn} = 3/2$  to the ferromagnetic region of  $B_{hf}$  allowed the extrapolation of  $B_{hf}$  values to 0 K, which are also shown in Table I.

The transition from ferromagnetic to antiferromagnetic order in each compound probably occurs due to the increase in the lattice parameter when temperature increases because Mn-Mn exchange interactions are strongly dependent on the  $c/a$  ratio of the crystal lattice.<sup>2</sup> As expected, the Néel temperature decreases when the concentration of Ge increases as more and more Si atoms are substituted with Ge in  $\text{LaMn}_2\text{Si}_2$  chiefly due to the increase in the Mn-Mn distance (Fig. 3). However, the behaviour of  $T_C$  is the opposite:  $T_C$  increases when the concentration of Ge increases,<sup>10</sup> as can

be seen in Table I. The transition temperatures are directly proportional to the exchange interaction constant  $J_{ex}$ , which is strongly dependent on the distance between the neighboring magnetic ions. Therefore,  $J_{ex}$  strongly changes its behaviour from ferromagnetic to antiferromagnetic regions when Ge concentration increases. An alternative explanation would be due to the strength of the superexchange interaction via Mn-Si(Ge)-Mn which depends on the bond angle between two Mn ions; however, this angle does not appreciably change with Ge concentration as can be seen in Table I.

#### IV. SUMMARY

The temperature dependence of  $B_{hf}(T)$  at Mn sites in  $\text{LaMn}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  compounds ( $0 \leq x \leq 1$ ) showed the expected behaviour for the host magnetization with a transition from ferromagnetic to antiferromagnetic order for all compounds and allowed the determination of  $T_N$  with accuracy. It was observed that  $T_N$  decreases when Ge concentration increases in an inverse evolution of that previously observed for the Curie temperature. This significant change in the behaviour of the transition temperatures is due to the increase in the Mn-Mn distance when Ge gradually replaces Si and was ascribed to a change in the exchange interaction constant  $J_{ex}$ .

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<sup>1</sup>K. S. V. L. Narasimhan, V. U. S. Rao, R. L. Bergner, and W. E. Wallace, *J. Appl. Phys.* **46**, 4957 (1975).

<sup>2</sup>I. Nowik, Y. Levi, I. Felner, and E. R. Bauminger, *J. Magn. Magn. Mater.* **147**, 373–384 (1995).

<sup>3</sup>R. Mallik, E. V. Sampathkumaran, and P. L. Paulose, *Appl. Phys. Lett.* **71**, 2385 (1997).

<sup>4</sup>T. Zhang, Y. Chen, Y. Tang, E. Zhang, and M. Tu, *Phys. Lett. A* **354**, 462–465 (2006).

<sup>5</sup>S. A. Granovsky, I. Yu. Gaidukova, M. Doerr, M. Loewenhaupt, and A. S. Markosyan, *Physica B: Condensed Matter* **391**, 79–87 (2007).

<sup>6</sup>E. V. Sampathkumaran, L. C. Gupta, R. Vijayaraghavan, Le Dang Khoi, and P. Veillet, *J. Phys. F: Met. Phys.* **12**, 1039–1043 (1982).

<sup>7</sup>A. W. Carbonari, R. N. Saxena, W. Pendl, Jr., J. Mestnik-Filho, R. N. Atilli, M. Olzon-Dionysio, and S. D. de Souza, *J. Magn. Magn. Mater.* **163**, 313–321 (1996).

<sup>8</sup>G. A. Cabrera-Pasca, A. W. Carbonari, B. Bosch-Santos, J. Mestnik-Filho, and R. N. Saxena, *J. Phys.: Condens. Matter* **24**, 416002 (2012).

<sup>9</sup>A. W. Carbonari, J. Mestnik-Filho, R. N. Saxena, and M. V. Lalić, *Phys. Rev. B* **69**, 144425 (2004).

<sup>10</sup>B. Bosch-Santos, A. W. Carbonari, G. A. Cabrera-Pasca, M. S. Costa, and R. N. Saxena, *J. Appl. Phys.* **113**, 17E124 (2013).