Antiferromagnet-ferromagnet transitions in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys induced by composition, magnetic field, and temperature

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Temperature and magnetic-field dependences of zero-field-cooled (ZFC) Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys with a distinctly layered crystal structure have been studied. At 4.2 K, alloys with $x<0.1$ show an antiferromagnetic state, which can be irreversibly transformed to a ferromagnetic state by a magnetic field. In contrast, ZFC alloys with $x\geq 0.1$ already have a ferromagnetic state. All alloys being in ferromagnetic state then exhibit a temperature-induced first-order ferromagnet $\rightarrow$ antiferromagnet transition at T_{tr}. ZFC $Gd_5(Si_xGe_{4-x})$ alloys with either antiferromagnetic or ferromagnetic initial state at 4.2 K also exhibit a second-order reversible antiferromagnet $\leftrightarrow$ paramagnet transition at the Néel temperature $T_N\approx 128$ K. Magnetic phase transition induced by a magnetic field at T_{tr} is determined by the exchange interactions between Gd magnetic moments located in the nearest slabs rather than those located in the same slab and can be described by Landau model of antiferromagnets. Similar magnetic correlations between Gd magnetic moments in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys can be induced either by the internal (composition) or by the external (magnetic field, temperature, and hydrostatic pressure) effects. It is likely that dipole-dipole interactions between magnetically ordered nearest slabs contribute to magnetic phase transitions.

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I. INTRODUCTION

Magnetic-field-induced transition from antiferromagnetic (AFM) to ferromagnetic (FM) state, AFM $\rightarrow$ FM transition, is observed for a variety of metallic and nonmetallic materials and belongs to one of the most interesting magnetic phenomena.[1,2] Such transition, also called as metamagnetic transition, takes place at or above a certain critical magnetic field, H_{cr}, and after the magnetic field is removed, the material typically returns to the initial AFM state, indicating that only fully reversible magnetic transition is involved. AFM $\rightarrow$ FM transition is sensitive to the magnetocrystalline anisotropy and exchange interactions, and shows continuous character for isotropic Heisenberg antiferromagnet or nearly discontinuous character for anisotropic Ising antiferromagnet. Experimental data and theoretical models describing metamagnetic transitions (see, for example, correlated-electron theory by Held *et al.*[3] or the XXZ model with next-to-nearest-neighbor coupling by Gerhardt *et al.*[4]) show that they are particularly interesting in the systems with anisotropic exchange interactions.

The most fascinating materials are those where AFM $\rightarrow$ FM transition induced by a magnetic field is coupled with a change in the crystal structure. Such a transition is first order in nature, is accompanied by heat release or absorption (see, for example, Bean and Rodbell[5]), exhibits interesting magnetic and electronic phenomena, and is observed in various metallic and nonmetallic materials including intermetallic compounds,[6–8] manganese and cobalt oxides with layered crystal structure.[7,9–11] The transition typically is irreversible, i.e., after the magnetic field is removed, the material remains in a ferromagnetic state. However, both reversible and irreversible AFM $\rightarrow$ FM transitions are observed for Gd_5Ge_4, which is one of the most interesting lanthanide-based binary compounds.[6,8,12,13]

Gd_5Ge_4 represents the Ge end of the $Gd_5(Si_xGe_{4-x})$ series while the opposite end is represented by Gd_5Si_4.[12,14] Gd_5Si_4 is a ferromagnet with a Curie temperature $T_C=335\pm 5$ K,[14] Gd_5Ge_4 is an antiferromagnet with a Néel temperature $T_N\approx 130$ K but only if cooled in a magnetic field less than a critical value of 8 kOe; note that its magnetic properties are very sensitive to the magnetic field, temperature, and direction of change, i.e., cooling or heating.[15]

Due to high sensitivity of the magnetic state of Gd_5Ge_4 to the magnetic field and temperature, magnetic correlations are sensitive to a very small substitution of Ge for Si; e.g., $Gd_5(Si_{0.4}Ge_{3.6})$, where 4.4 at. % of Ge atoms are substituted for Si atoms, shows ferromagnetic state below $\sim$80 K.[16] As because the ground state of $Gd_5(Si_xGe_{4-x})$ alloy with $x\geq 0.4$ is ferromagnetic, the exchange interactions between the Gd magnetic moments can be changed from antiferromagnetic to ferromagnetic by a small Ge $\rightarrow$ Si substitution, i.e., when $0<x<0.4$. The crystal structure of Gd_5Ge_4 is formed by a $\sim$0.5 nm-thick flat fragment (slabs) consisting of three layers of Gd and two layers of Ge atoms (details were discussed by Choe *et al.*[17] and Pecharsky *et al.*[18]); therefore, the exchange interactions between Gd atoms appear to be anisotropic. It was suggested by Levin *et al.*[15] that Gd magnetic moments in each slab are mostly coupled ferromagnetically while two nearest slabs are coupled antiferromagnetically and this suggestion was confirmed by a neutron-scattering experiment.[19] The origin of ferromagnetism and antiferromagnetism in Gd_5Ge_4 has also been discussed by Paudyal *et al.*[20]

Generally, one can expect that even a small change in the Si/Ge ratio can significantly impact the exchange interactions between Gd atoms in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys within each slab, J', and particularly between them, J''. Such exchange interactions were observed for Landau antiferromagnets, e.g., $FeCl_2$ and $CoCl_2$ layered compounds.[21]

The competition between J', J'', and magnetocrystalline anisotropy can result in complex temperature and magnetic-field dependences of the magnetization and provide impor-

tant information about magnetic correlations in low-dimensional magnetic systems. Note also that the two types of Gd-Gd exchange interactions were suggested for the $Gd_5(Si_xGe_{4-x})$ alloys,[22] Ruderman-Kittel-Kasuya-Yoshida via conduction electrons, and superexchange via Si(Ge) atoms, and, therefore, both can be sensitive to the Si/Ge ratio. In this paper, the effect of the Si/Ge ratio, magnetic field, and temperature on the magnetization of $Gd_5(Si_xGe_{4-x})$ alloys with $0 \leq x \leq 0.4$ has been studied. It was found that in these alloys, the magnetic field may have a similar effect on the magnetic correlations between Gd magnetic moments as the composition.

II. EXPERIMENTAL DETAILS

Polycrystalline $Gd_5(Si_xGe_{4-x})$ alloys with $x=0.02$, 0.6, 0.1, 0.2, 0.3, and 0.4 were prepared by arc melting of the mixture of constituent elements using high-purity Gd (99.9 +at. %), Ge (99.99+at. %), and Si (99.99+at. %). The Gd was prepared by the Materials Preparation Center at the Ames Laboratory and contained the following major impurities (in atomic ppm): O-440, C-200, H-160, N-90, Fe-40, and F-30. The Ge and Si were purchased from Meldfrom Metals and CERAC Inc., respectively. The total weight of each arc-melted button was ~10 g and weight losses after arc melting did not exceed 0.5%. No impurity phases were detected by x-ray powder diffraction of the as-cast $Gd_5(Si_xGe_{4-x})$ alloys. All measurements were carried out using the as-prepared alloy. Isothermal and isofield magnetic measurements were performed in the temperature range of 4.2–200 K and dc magnetic fields up to 50 kOe using a Lake Shore Magnetometer model 7525; the error of magnetic measurements was ~2%.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Phase transformations in alloys with antiferromagnetic initial state

At room temperature, Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys have the Gd_5Ge_4-type *Pnma* crystal structure earlier reported for Gd_5Ge_4.[12,13] Within experimental error, lattice parameters of Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys slightly decrease with the Si content. Such a change in lattice parameter is due to smaller atomic size of Si atoms compared to that of Ge atoms and was observed for Si-rich $Gd_5(Si_xGe_{4-x})$ alloys.[8] Hence, the substitution of Si for Ge in these alloys produces the effect of "chemical pressure" on the crystal lattice resulting in a decrease in Gd-Gd distances.

Figure 1 shows the magnetization of the zero-field-cooled (ZFC) Gd_5Ge_4, $Gd_5(Si_{0.02}Ge_{3.98})$, and $Gd_5(Si_{0.06}Ge_{3.94})$ measured at 4.2 K. The magnetization of Gd_5Ge_4 reflects AFM $\rightarrow$FM transition at $H_{cr} \approx 19$ kOe as it was reported in Ref. 6. The transition is fully irreversible, i.e., after the magnetic field is reduced, the sample remains in the ferromagnetic state. Despite the absence of a significant single-ion anisotropy of Gd ions, AFM $\rightarrow$FM transition observed for Gd_5Ge_4 during the first application of the magnetic field is typical of metamagnetic transition of anisotropic Ising-type AFM.[1,2] Magen *et al.*[23] showed that a coupled crystallographic

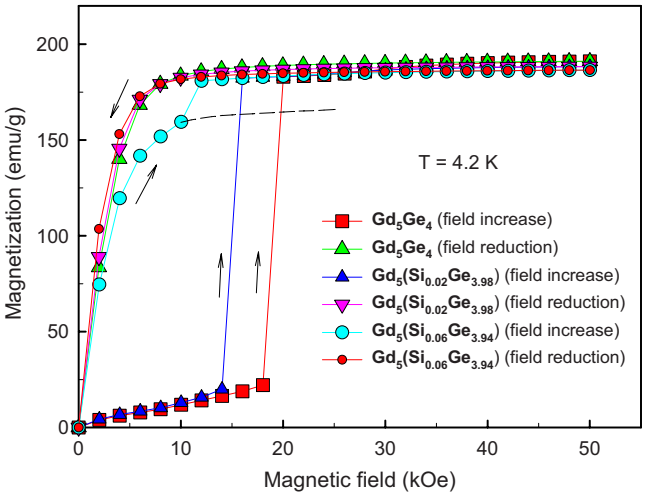

FIG. 1. (Color online) Magnetization of ZFC $Gd_5(Si_xGe_{4-x})$ alloys with $0 \leq x \leq 0.06$ at 4.2 K. The expected behavior of the magnetization of $Gd_5(Si_{0.06}Ge_{3.94})$ without following AFM $\rightarrow$FM transition is shown by the dashed line.

transition—magnetic transition from antiferromagnetic Gd_5Ge_4-type *Pnma* to ferromagnetic Gd_5Si_4-type *Pnma*, can be induced by a magnetic field. A similar AFM $\rightarrow$FM transition also takes place in $Gd_5(Si_{0.02}Ge_{3.98})$ (see Fig. 1) but the critical magnetic field is smaller, $H_{cr} \approx 15$ kOe. Note that the substitution of Ge for Si results not only in chemical pressure but possibly also affects chemical bonding between the slabs; the concept of forming and breaking covalent bonds in $Gd_5(Si_2Ge_2)$ during the first-order ferromagnet $\leftrightarrow$ paramagnet transition was discussed by Choe *et al.*[17] Furthermore, it is very likely that such a transition is a universal phenomenon for magnetically ordered materials with layered crystal structure: similar transitions were observed for quite different materials, e.g., intermetallic alloys,[8] mixed-valence manganites,[9,11] and cobaltites[10] (see also interesting data and analysis of metamagnetic transitions observed by Hardy *et al.*[7] in Gd_5Ge_4 and $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$).

The magnetization of $Gd_5(Si_{0.06}Ge_{3.94})$ exhibits even more interesting behavior: a ferromagneticlike dependence in low magnetic field with the following steplike increase in ~11 kOe is observed. The behavior of the magnetization of $Gd_5(Si_{0.06}Ge_{3.94})$ can be understood if one assumes that at 4.2 K a big fraction, ~90%, of ZFC $Gd_5(Si_{0.06}Ge_{3.94})$ sample was already transformed into a FM state during cooling (the expected behavior of the magnetization without the following magnetic-field-induced transition shown in Fig. 1 by the dashed line). The remaining fraction, ~10%, of $Gd_5(Si_{0.06}Ge_{3.94})$ initially was in a AFM state but then has been transformed into a FM state by the application of a magnetic field $H_{cr} \approx 10$ kOe. During the second application of a magnetic field (not shown in Fig. 1), the magnetization of all three $Gd_5(Si_xGe_{4-x})$ alloys follows the first demagnetization path, indicating that they have a FM state, i.e., AFM $\rightarrow$FM transition is irreversible.

Data for ZFC $Gd_5(Si_{0.06}Ge_{3.94})$ alloy show that both the AFM and FM phases coexist at 4.2 K, indicating that even a very small substitution of Ge atoms for Si atoms strongly affects magnetic correlations between Gd atoms. The coex-

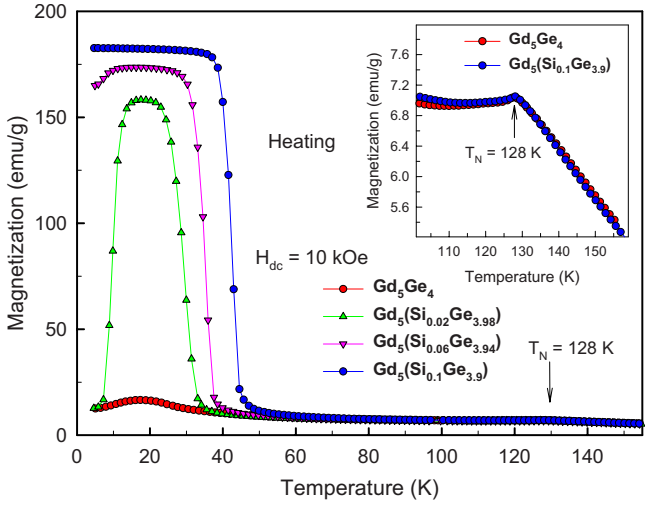

FIG. 2. (Color online) Temperature dependencies of the magnetization of ZFC $Gd_5(Si_xGe_{4-x})$ alloys with $0 \leq x \leq 0.1$ measured on heating in a 10 kOe magnetic field. The inset shows an expanded view of the magnetization of Gd_5Ge_4 and $Gd_5(Si_{0.1}Ge_{3.9})$ between 100 and 160 K.

istence of ferromagnetic and antiferromagnetic phases, e.g., a magnetically heterogeneous or magnetic-phase-separated state, is only one of the many intriguing phenomena observed for the Gd_5Ge_4-based alloys.[8,15] Note that magnetic-phase-separated state was also found in complex oxides, $Pr_{0.5}Ca_{0.2}Sr_{0.3}MnO_3$ (Ref. 9) and $La_{1-x}Sr_xCoO_3$,[10] and currently attracts big attention. However, magnetically heterogeneous state in Gd_5Ge_4 can be formed only if the sample was cooled in a magnetic field above ~8 kOe but below ~18 kOe.[8] Relatively large Ge atoms result in volume expansion and enhance antiferromagnetic coupling, while small Si atoms result in volume compression and enhance ferromagnetic exchange. The coexistence of both AFM and FM phases in ZFC $Gd_5(Si_{0.06}Ge_{3.94})$ indicates (i) the presence of magnetic-phase-separated state and (ii) a similar influence of the *composition* and *magnetic field* on the development and stability of ferromagnetically and antiferromagnetically ordered phases in Gd-rich $Gd_5(Si_xGe_{4-x})$ alloys. Hence, it is possible to form ~100% of a FM phase at 4.2 K by cooling Gd_5Ge_4 in a magnetic field of ≥18 kOe, or by the application of 19 kOe magnetic field at 4.2 K to ZFC sample, or by the substitution of about 0.66 at. % of Ge atoms for Si. Note that the FM state begins partially to develop during cooling in the $Gd_5(Si_{0.06}Ge_{3.94})$ alloy. The process of magnetization of Gd-rich $Gd_5(Si_xGe_{4-x})$ alloys in the FM state does not depend on the Si/Ge ratio, indicating a similar domain structure and nearly the same, ~10 kOe, field of saturation of all alloys.

Figure 2 shows temperature dependencies of the magnetization of ZFC Gd_5Ge_4, $Gd_5(Si_{0.02}Ge_{3.98})$, $Gd_5(Si_{0.06}Ge_{3.94})$, and $Gd_5(Si_{0.1}Ge_{3.9})$ measured on heating in a 10 kOe magnetic field. The magnetization of Gd_5Ge_4 demonstrates a small, a few emu/g, peak at 19 K, while the magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ exhibits a large peak, 155 emu/g, with the center at the same temperature. A similar peak was observed for Gd_5Ge_4 in a 16 kOe magnetic field, where the low-temperature part of the peak reflects the AFM→FM transformation and the high-temperature part indicates the reverse FM→AFM transformation. The ferromagneticlike state of these alloys exists in the narrow temperature interval and its width depends on the applied magnetic field.

The magnetization shown in Fig. 2 indicates that in a 10 kOe magnetic field, a large fraction, 97%, of $Gd_5(Si_{0.06}Ge_{3.94})$ sample is in the ferromagnetic state while $Gd_5(Si_{0.1}Ge_{3.9})$ is completely ferromagnetic. When the temperature increases, the magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ drops from ~180 emu/g at 38 K to ~10 emu/g at 46 K, indicating that FM→AFM transition takes place at an average temperature of 42 K. The temperature of the transition, T_{tr}, can be associated with the Curie temperature, T_C, and with the average temperature when FM→AFM transformation begins and ends. Because FM→AFM transition in Gd_5Ge_4 above ~20 K is first order in nature,[8] two magnetically ordered phases, ferromagnetic and antiferromagnetic, coexist in the vicinity of phase transformation, forming magnetically a phase-separated state.

The substitution of Ge for Si in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys enhances the ferromagnetic order increasing both the magnetization at 4.2 K and the temperature of a first-order phase transition from the FM to the AFM state. A small increase in the magnetization of $Gd_5(Si_{0.06}Ge_{3.94})$, when the temperature rises from 4.2 to ~10 K (see Fig. 2), agrees well with the isothermal dependence of the magnetization vs magnetic field at 4.2 K (see Fig. 1). Furthermore, this shows that the temperature induces the transformation of a small fraction (less than 10%) of AFM phase remaining in ZFC $Gd_5(Si_{0.06}Ge_{3.94})$ into FM phase.

The magnetization of all Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys studied so far exhibits a similar anomaly around 130 K, which is practically independent of the alloy composition. The inset in Fig. 2 shows the expanded view between 100 and 160 K of the magnetization of ZFC Gd_5Ge_4 and $Gd_5(Si_{0.1}Ge_{3.9})$ measured in the 10 kOe magnetic field. Although Gd_5Ge_4 is the low-temperature antiferromagnet while $Gd_5(Si_{0.1}Ge_{3.9})$ is the low-temperature ferromagnet, the magnetization of both alloys between 100 and 160 K is very similar and indicates the same Néel temperature of ~128 K. Note that a similar $T_N \approx 127$ K was reported by Morellon *et al.*[16] for $Gd_5(Si_{0.4}Ge_{3.6})$. The inverse magnetic susceptibility, $1/\chi$, of $Gd_5(Si_xGe_{4-x})$ with $0 \leq x \leq 0.4$ measured in the 10 kOe magnetic field, increases linearly above ~170 K and can be fitted by the Curie-Weiss law. All of these alloys have similar positive Curie-Weiss temperature, $\theta_p \approx 94$ K, which was reported earlier for Gd_5Ge_4.[7] In the temperature range of 140–170 K, the inverse magnetic susceptibility has a nonlinear character, indicating that a short-range magnetic order occurs in $Gd_5(Si_xGe_{4-x})$ just above the Néel temperature.

Figure 3 shows temperature dependencies of the magnetization of ZFC samples measured during heating at various conditions. The magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ at 4.2 K is very similar when measured in 5 kOe, i.e., ~10 emu/g, indicating a low-magnetized state [Fig. 3(a)]. However, it shows quite different temperature dependence when measured in 10 kOe magnetic fields. An increase in the magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ by ~700% was observed when temperature was changed by ~8 K; this shows a sharp development of a high-magnetized state induced by tempera-

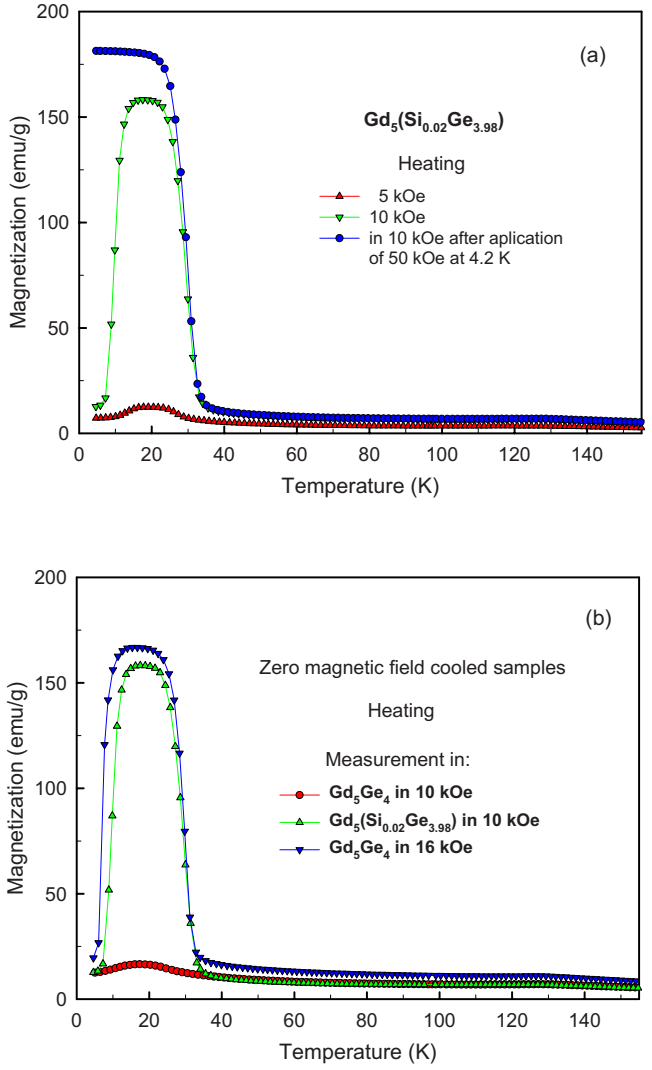

FIG. 3. (Color online) Temperature dependencies of the magnetization of (a) ZFC $Gd_5(Si_{0.02}Ge_{3.98})$ measured on heating under various conditions and (b) ZFC Gd_5Ge_4 and $Gd_5(Si_{0.02}Ge_{3.98})$ measured on heating in 10 and 16 kOe magnetic fields.

ture in a 10 kOe magnetic field, while in 5 kOe the alloy remains in a low-magnetized state. Figure 3(a) also shows temperature dependence of the magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ measured in a 10 kOe magnetic field after the alloy was completely transformed from the AFM state into the FM state by the application of 50 kOe magnetic field at 4.2 K. Note that the temperature of FM→AFM transformation is approximately the same, ~34 K, whether $Gd_5(Si_{0.02}Ge_{3.98})$ at 4.2 K was in the AFM state or initially transformed to the FM state. In contrast, the value of maximal magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ at ~20 K depends on the sample history: the magnetization of the sample, which initially was in the AFM state, is smaller than that of the same sample, which initially was in the FM state. Such a behavior demonstrates that temperature cannot totally transform a AFM state of the sample into a FM state during measurements in a 10 kOe magnetic field. Figure 3(b) compares the temperature dependencies of the magnetization of Gd_5Ge_4 and $Gd_5(Si_{0.02}Ge_{3.98})$ measured in 10 and 16 kOe magnetic fields. As mentioned above, the magnetization of Gd_5Ge_4 in the 10 kOe magnetic field has only a small broad maximum of ~10 emu/g, while in a 16 kOe magnetic field it exhibits a peak of ~155 emu/g. It is quite intriguing that a similar peak is observed for the magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ measured in a 10 kOe magnetic field. In addition, small peaks of ~10 emu/g in the magnetization are observed at ~20 K for both $Gd_5(Si_{0.02}Ge_{3.98})$ and Gd_5Ge_4 alloys when measured in 5 kOe [Fig. 3(a)] and 10 kOe [Fig. 3(b)] magnetic fields, respectively. Hence, a similar temperature dependence of correlations between Gd magnetic moments in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys can be determined by a composition or by a magnetic field.

Temperature dependencies of the total magnetization of the $Gd_5(Si_xGe_{4-x})$ antiferromagnetic alloys below ~30 K [see Figs. 3(a) and 3(b)] reflect a change in orientation of magnetic moments of two nearest slabs. Magnetic moments of Gd in each slab are oriented along the **c** or **b** direction when alloys are in the AFM or FM state, respectively.[15] This means that antiparallel magnetic moments of two neighboring slabs forming the AFM state change their orientations in applied magnetic field with temperature, forming parallel orientation and thus the FM state. Hence, both the composition and magnetic field can develop a similar alignment of Gd magnetic moments located in two nearest slabs in ZFC Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys. Note that **a** and **c** lattice parameters of $Gd_5(Si_xGe_{4-x})$ decrease approximately by 0.11% while the **b** parameter decreases by about 0.06% when x changes from 0 to 0.4. Furthermore, **a** and **c** lattice parameters are responsible mostly for the exchange interactions within each slab while the **b** parameter mostly affects those between neighboring slabs. Because the Néel temperature of ~130 K depends weakly on the Si content in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys, one may suggest that the distance between the nearest slabs and the type of atoms located on the surface of each slab, e.g., Ge or Si, are crucial for the development of a three-dimensional (3D) ferromagnetic order in these alloys.

Figure 4 shows the critical magnetic field, H_{cr}, and transition temperature, T_{tr}, of the AFM→FM transition at 4.2 K vs the Si content in ZFC Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys. Note that at 4.2 K, ZFC alloys with $0 \leq x \leq 0.04$ exhibit a completely antiferromagnetic state, while alloys with $0.06 \leq x \leq 0.1$ have a mixed antiferromagnetic state—ferromagnetic state or completely ferromagnetic state. However, the critical magnetic field independently of the initial magnetic state of ZFC alloys at 4.2 K decreases nearly linearly with the Si content at a rate of ~18 kOe/at. % Si. The zero critical magnetic field, which means fully 3D ferromagnetic state occurring in ZFC alloy, is expected for the composition with $x \approx 0.1$. The transition temperature measured on heating increases nearly linearly at the rate of ~13 K/at. % Si. Note that T_{tr} for the alloy with $x \approx 0.1$, which is fully ferromagnetic at 4.2 K, is expected to be 42 K (see open triangle in Fig. 4). Both dependencies show that the initial antiferromagnetic coupling decreases while the ferromagnetic coupling increases with the Si content.

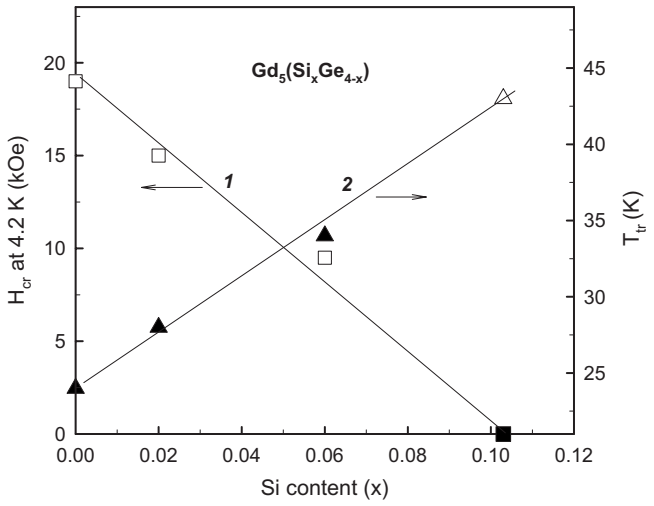

FIG. 4. (1) The critical magnetic field, H_{cr}, at 4.2 K and (2) temperature of FM→AFM transition, T_{tr}, measured in a 10 kOe magnetic field on heating ZFC $Gd_5(Si_xGe_{4-x})$ alloys with $0 \leq x \leq 0.1$. Filled square shows $x \approx 0.1$ for expected $H_{cr}=0$, open triangle shows expected T_{tr} for this composition. Note that Gd_5Ge_4 before the measurements was transformed into a FM state by the application of a magnetic field up to 50 kOe at 4.2 K (see Fig. 1).

B. Phase transformations in alloys with ferromagnetic initial state

Figure 5 shows magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ alloy measured at 4.2 K. Magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ at 4.2 K shows ~100% ferromagnetic state of the sample. This agrees well with the magnetization expected from H_{cr} vs the Si content dependence (see Fig. 4 and the text above). The saturation magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ at 4.2 K is practically the same as observed for Gd_5Ge_4 after it was transformed into the ferromagnetic state (see Fig. 1). The calculated effective magnetic moment in the saturated state is ~7.3 μ_B/Gd atom, indicating a nearly collinear orientation

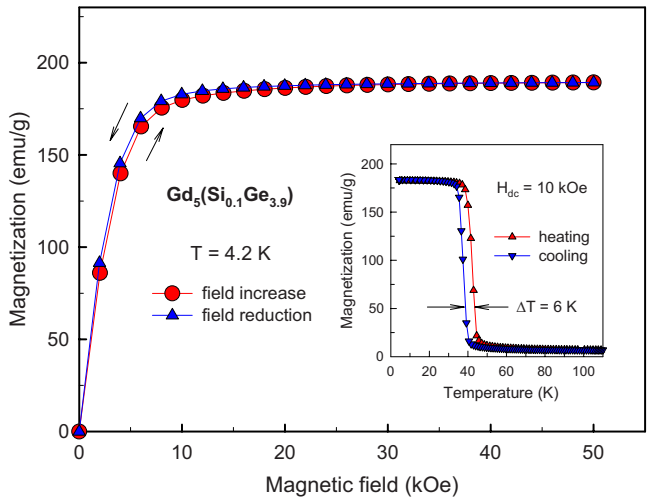

FIG. 5. (Color online) Magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ measured at 4.2 K. The inset shows temperature dependence of the magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ measured in a 10 kOe magnetic field upon heating and cooling.

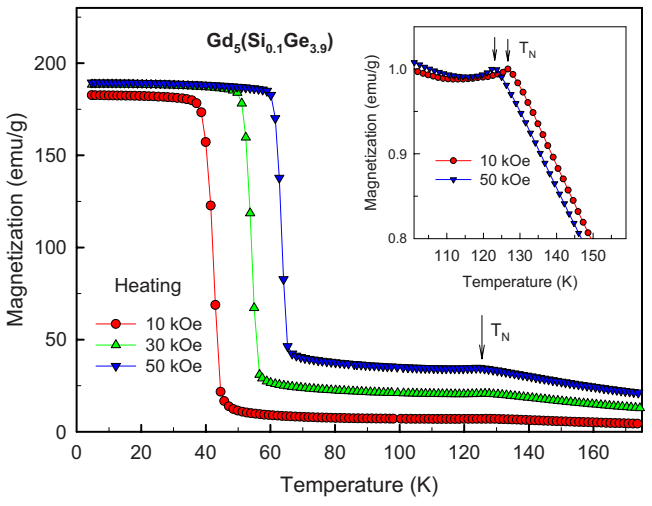

FIG. 6. (Color online) Temperature dependence of the magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ measured on heating in magnetic fields varying between 10 and 50 kOe. The inset shows an expanded view of the magnetization measured in 10 and 50 kOe magnetic fields between 100 and 160 K.

of the Gd magnetic moments similar to that reported for Gd_5Ge_4.[7,15] It is very likely that at 4.2 K, the magnetic structure of both ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ and transformed Gd_5Ge_4 is similar. Hence, one can suggest that magnetic correlations in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys depend strongly on a chemical pressure and an applied magnetic filed. Effect of pressure on Gd_5Ge_4 has been studied by Magen *et al.*[23] and was shown that the ferromagnetic state of Gd_5Ge_4 at 5 K can be induced by the application of hydrostatic pressure. The fraction of induced ferromagnetic phase depends on the pressure, and nearly 100% of the initial AFM phase of ZFC Gd_5Ge_4 can be transformed into FM phase by applying a hydrostatic pressure of ~11 kbar.[23]

The inset in Fig. 5 shows the temperature dependence of the magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ during heating and cooling. Both the curves reveal the transformation between AFM and FM phases, which occurs at ~40 K and supports the conclusion that ferromagnetic state in $Gd_5(Si_{0.1}Ge_{3.9})$ is developing during cooling in a zero magnetic field. This is quite different compared to Gd_5Ge_4, where a ferromagnetic state develops only if the sample is cooled in a 20 kOe magnetic field.[8] The magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ shows a temperature hysteresis of ~6 K, which is one of classical intrinsic features of a first-order transition and was also observed for the Si-rich $Gd_5(Si_xGe_{4-x})$ alloys in the vicinity of the phase transformations. So, $Gd_5(Si_{0.1}Ge_{3.9})$ cooled in zero magnetic field shows ferromagnetic order with $T_C \approx 40$ K while Gd_5Ge_4 exhibits a similar T_C when cooled in a 20 kOe magnetic field.

Figure 6 shows temperature dependencies of the magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ alloy measured in the 10, 30, and 50 kOe magnetic fields. Magnetization of ZFC $Gd_5(Si_{0.1}Ge_{3.9})$ at 4.2 K shows ~100% ferromagnetic state of the sample. This agrees well with the magnetization expected from H_{cr} vs the Si content dependence (see Fig. 4 and the text above). The saturation magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ at 4.2 K is practically the same as observed

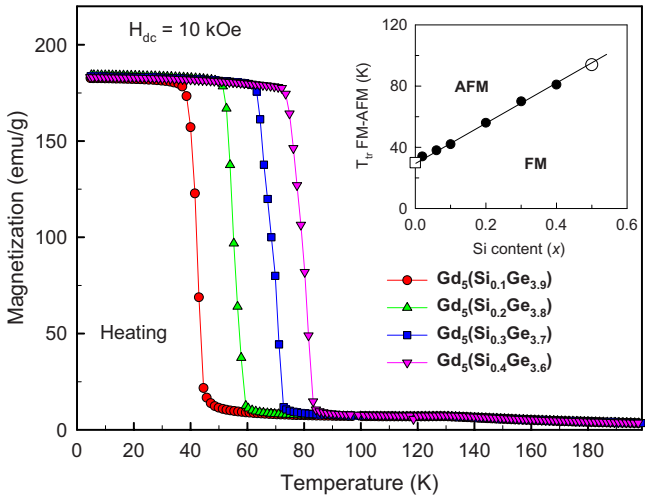

FIG. 7. (Color online) Temperature dependence of the magnetization of ZFC $Gd_5(Si_xGe_{4-x})$ alloys measured in a 10 kOe magnetic field during heating. The inset shows temperature dependence of the FM→AFM transition as a function of the Si content. The open square and open circle, indicate T_{tr} for $Gd_5(Si_xGe_{4-x})$ alloys with $x=0$ and 0.5 (Ref. 16), respectively.

for Gd_5Ge_4 after it was transformed into the ferromagnetic state (see Fig. 1).

According to Fig. 6, FM→AFM transition is shifting toward higher temperatures by a magnetic field at a rate of ~0.5 K/kOe showing that the magnetic field enhances the ferromagnetic state, which is in good agreement with the magnetic diagram of Gd_5Ge_4.[24,25] The inset in Fig. 6 shows an expanded view between 100 and 160 K of the magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ measured in both 10 and 50 kOe magnetic fields. Both curves exhibit a peak at 128 and 123 K when measured in both 10 and 50 kOe magnetic fields, respectively. Such a dependence of the magnetization is typical for a second-order phase transition between low-temperature antiferromagnetic and high-temperature paramagnetic phases. The magnetization of $Gd_5(Si_{0.1}Ge_{3.9})$ increases when temperature decreases below T_N, which is not typical for common antiferromagnets and shows the effect of long-range interactions between ferromagnetically ordered two-dimensional (2D) slabs. So, it is enough to substitute only ~1 at. % of Ge in Gd_5Ge_4 for Si to form a 3D ferromagnetic ordering with the following first-order FM→AFM transition at ~42 K; a second-order AFM→PM transition is still observed at a similar T_N, i.e., at ~130 K.

Figure 7 shows temperature dependencies of the magnetization of $Gd_5(Si_xGe_{4-x})$ with $0.1 \le x \le 0.4$; all samples have fully ferromagnetic state if cooled in the zero magnetic field. Measurements conducted in the same 10 kOe magnetic field show that the temperature of the FM→AFM transition increases with increasing Si content. The inset in Fig. 7 shows that T_{tr} of $Gd_5(Si_xGe_{4-x})$ alloys increases nearly linearly with the Si content at a rate of ~12 K/at. % Si, which is similar to that observed for alloys with $0 \le x \le 0.1$ (see the text above). The open square shows T_{tr} for Gd_5Ge_4 obtained on heating after FM state was induced irreversibly by the application of 50 kOe magnetic field at 4.2 K. The open circle shows the temperature of the FM→AFM transition for $Gd_5(Si_{0.5}Ge_{3.5})$ from Ref. 16. For a sample with $x \approx 0.75$, one can expect the presence of a critical point where all three phases, AFM, FM, and PM may coexist depending on the temperature and the magnetic field. Furthermore, both the FM→AFM and AFM→PM magnetic phase transitions could merge for the alloy with $x \approx 0.75$. The data do not support the analytical result by Held *et al.*[3] for anisotropic antiferromagnets that metamagnetic transitions can be changed from a first order at low temperatures to a second order near the Néel temperature. It is well known that temperature-induced ferromagnet↔paramagnet transitions observed in the Si-rich $Gd_5(Si_xGe_{4-x})$ alloys at high temperatures are of first order in nature. Magnetic and structural transitions in these alloys are strongly coupled together forming a magnetoelastic system with high sensitivity to temperature and magnetic field. Similar first-order transitions are also observed for Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys but they occur below 130 K and they are between ferromagnetic and antiferromagnetic states.

C. Temperature of magnetic phase transitions vs the composition and magnetic field

Our data show that the temperature of FM→AFM transition, T_{tr}, of Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys with $0 \le x \le 0.4$ increases with the Si content at a rate of ~12 K/at. % Si. For Si-rich $Gd_5(Si_2Ge_2)$ alloy, this rate leads to $T_{tr}=296$ K, which is in good agreement with the value of 275 K observed by direct measurements. Also, T_{tr} of Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys with the initial ferromagnetic state increases with a magnetic field at a rate of ~0.5 K/kOe. In addition, the ferromagnetic state of ZFC Gd_5Ge_4 can be induced by pressure and then T_{tr} increases with applied pressure at a rate of ~4.9 K/kbar.[23] Therefore, data presented here and published earlier show that three quite different parameters, i.e., chemical composition, magnetic field, and pressure, can strongly affect exchange interactions in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys. A comparison of all these parameters shows that the substitution of 0.08 at. % of Ge for Si is equivalent to an applied hydrostatic pressure of 0.2 kbar and an applied magnetic field of 2 kOe. Both the Ge→Si substitution and hydrostatic pressure generally enhance the ferromagnetic state and decrease the volume of the $Gd_5(Si_xGe_{4-x})$ unit cell. Hence, the effect of a magnetic field is similar to that produced by the composition and hydrostatic pressure, i.e., both compress the lattice.

Below 130 K, each slab in Gd_5Ge_4 is ordered ferromagnetically forming a 2D ferromagnetic system.[15] Each elemental unit of Gd_5Ge_4 consists of two ferromagnetic slabs coupled antiferromagnetically forming a 3D antiferromagnetic system. Therefore, the AFM→FM transition in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys induced by a magnetic field should be viewed as a transition from a 2D to a 3D ferromagnetic state. One of the models describing an antiferromagnetic state was proposed by Landau[21] and uses a combination of two antiferromagnetically coupled ferromagnetic planes. This model has been applied to antiferromagnetic materials with a distinctly layered crystal structure, i.e., $FeCl_2$ and $CoCl_2$,[1] where each layer of 3*d* ions is ordered ferromagnetically

while the two nearest layers are coupled antiferromagnetically. Ferromagnetic slabs, as flat fragments composing the elemental unit of these alloys, should be considered as a ferromagnetic plane in Landau model.[21] Exchange interactions between the Gd ions in the Gd-rich $Gd_5(Si_xGe_{4-x})$ alloys include both the intraslab ferromagnetic and interslab antiferromagnetic interactions, J' and J'', respectively. Because the Néel temperature of these alloys, ~130 K, is practically independent of the Si/Ge ratio, one can conclude that the intraslab ferromagnetic J' interaction is insensitive to composition. In spite of that, the decrease in a critical magnetic field with the Si content shows that the magnitude of J'' also decreases. Hence, critical magnetic fields of a AFM $\rightarrow$FM transition and a FM$\rightarrow$AFM transition in $Gd_5(Si_xGe_{4-x})$ are determined by the interslab interaction rather than by an intraslab exchange interaction. While J' is relatively large and constant, ~11 meV as estimated from T_N value, J'' depends on the Si/Ge ratio and increases from 2.4 to 3.2 meV for $x=0.02$ and 0.1, respectively, as estimated from T_{tr}. Each slab of Gd_5Ge_4-based alloys can be considered as a 2D magnetic system ordered ferromagnetically. In the AFM state, the magnetic moments of two nearest slabs of the unit cell are oriented in opposite directions. Hence, it is likely that two nearest slabs attract each other due to dipole-dipole interactions. In the FM state, the magnetic moments of two nearest slabs, instead of being oriented in the same direction and repel each other, can be oriented perpendicular to the slabs, i.e. be aligned along the **b** direction as it was shown for Gd_5Ge_4.[15] Hence, the magnetic-field-induced transition, when measured at constant temperature, or the temperature-induced transition, when measured in constant magnetic field, in Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys depends on the chemical bonding between atoms within the nearest slabs and probably on the magnetic dipole-dipole interactions between them.

IV. CONCLUSIONS

All Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys with $0 \leq x \leq 0.4$ show a second-order AFM$\leftrightarrow$PM phase transition at the Néel temperature of ~130 K. Depending on the composition, the magnetic ground state of these alloys cooled in a zero magnetic field can be either antiferromagnetic or ferromagnetic. While the magnetically heterogeneous state (or phase-separated state) in Gd_5Ge_4 at 4.2 K can be formed during cooling in a magnetic field between 10 and 18 kOe, a similar state is observed at 4.2 K for the zero-field-cooled $Gd_5(Si_{0.06}G_{3.94})$ alloy. The temperature of FM$\rightarrow$AFM transition in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys can be increased by a composition, magnetic field, or pressure; a similar influence is observed for (i) 0.08 at. % Ge$\rightarrow$Si substitution, (ii) 2 kOe applied magnetic field, and (iii) 0.2 kbar hydrostatic pressure. The same temperature dependence of the magnetization of $Gd_5(Si_{0.02}Ge_{3.98})$ and Gd_5Ge_5 is observed when the magnetization is measured in 10 kOe and 16 kOe magnetic fields, respectively. Hence, similar magnetic correlations between Gd magnetic moments in the Ge-rich $Gd_5(Si_xGe_{4-x})$ alloys can be affected either by the internal (composition) or external (magnetic field, temperature, or hydrostatic pressure) parameters. The antiferromagnetic state of these alloys can be described by the Landau model, where magnetic phase transformations induced by temperature and/or magnetic field below the Néel temperature are determined by the exchange interactions between Gd magnetic moments located in different slabs rather than those located within the same slab. It is very likely that magnetic dipole-dipole interactions between magnetic moments of nearest antiferromagnetically coupled slabs also contribute to the magnetic-field-induced AFM$\rightarrow$FM transition in Gd_5Ge_4-based alloys.

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