Magnetic correlations induced by magnetic field and temperature in Gd_5Ge_4

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Several unexpected and intriguing magnetic phenomena have been observed in the Gd_5Ge_4 compound. First, below ~130 K, Gd_5Ge_4 is antiferromagnetic in a zero magnetic field, but it can be transformed into the ferromagnetic state both irreversibly (below 10 K) and reversibly (above 20 K) depending on the magnitude of the applied magnetic field, the temperature, and the direction of their changes. Second, the irreversible antiferromagnetic→ferromagnetic transformation at 4.3 K is abrupt in magnetic fields exceeding 18 kOe, but it is sluggish in lower (~17 kOe) magnetic fields. Third, both the antiferromagnetic and ferromagnetic Gd_5Ge_4 phases may coexist indefinitely under certain combinations of the magnetic field and temperature. It is likely that the unusual magnetic correlations in Gd_5Ge_4 arise due to strongly anisotropic exchange interactions as a result of variations in the chemical bonding in this naturally layered, and therefore, low-dimensional magnetic system.

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I. INTRODUCTION

Low-dimensional magnetic systems draw considerable attention due both to their fundamental importance and existing practical applications.[1–9] The basic distinction arises from the competition between two-dimensional (2D) and 3D exchange interactions, which leads to the appearance of complex magnetic structures and, as a result, unusual magnetic properties. Practical applications of low-dimensional magnetic materials include superparamagnetic systems for high-density magnetic storage media and magnetic multilayers for magnetoresistive read heads and sensors. Among the numerous bulk low-dimensional magnetic systems, some of the most intriguing are $4f$-electron materials, where magnetic anisotropy, borne by either or both the lanthanide single-ion or the crystalline lattice anisotropy, varies considerably. Conventionally, low-dimensional $4f$-electron systems include materials containing Tb, Dy, Ho, and Er, i.e., the lanthanides with anisotropic single-ion exchange interactions, where a positive short-range exchange between the localized magnetic moments should favor 2D ferromagnetism, while a negative long-range exchange interaction may enhance 3D antiferromagnetism. Recently similar phenomena have been surprisingly observed in several Gd-based materials, i.e., in compounds where single-ion exchange is fundamentally isotropic [e.g., $Gd(Ni_{1-x}Cu_x)$,[10] GdCu,[11] and $Gd_{64}Sc_{36}$ (Ref. 12)], which points to the presence of an additional mechanism(s) for the anisotropy of interactions between the localized magnetic moments of Gd ions.

The increased complexity of lanthanide-based systems provides multiple degrees of freedom, enabling better control over the exchange interactions and, therefore, the magnetic properties of bulk materials. A recent example is found in the $Gd_5(Si_xGe_{4-x})$ system, where strongly interacting magnetic and non-magnetic ions are arranged in subnanometer-thick 2D fragments (slabs) forming a 3D crystallographic framework. The interslab interactions in these naturally occurring nanolayered magnetic materials may be controlled with a high precision by varying the stoichiometry (i.e., the value of x), and as a result, a variety of striking physical phenomena have been already discovered in this family of alloys. These include giant magnetocaloric effect,[13] giant magnetostriction,[14] unusual magnetism,[15] and spontaneously generated voltage[16] when $0 \leqslant x \leqslant 2$. All are due to the simultaneous magnetic and crystallographic (Martensitic) transformation reversibly induced by a magnetic field and/or temperature. During the transformation process covalentlike bonds between Si(Ge)-Si(Ge) atoms connecting neighboring slabs are broken or formed depending on the direction of the transformation.[17] It has been established that in the ferromagnetic state all of the slabs in $Gd_5(Si_xGe_{4-x})$ with $0<x \leqslant 4$ are connected through the Si (Ge) atoms.[18] In the paramagnetic state the character of the interslab bonding depends on the Si/Ge ratio, and for Gd_5Ge_4 $(x=0)$ at room temperature all of the interslab bonds are broken.[17–19]

As a result of weakened chemical interactions between the slabs, the intraslab exchange interactions may become considerably different from the interslab magnetic exchange. The 2D exchange is expected to dominate the magnetism of a slab, while the 3D interslab exchange should affect the long-range magnetic order and the resulting magnetic structure of the system. The magnetic structure remains undetermined for any of the $Gd_5(Si_xGe_{4-x})$ compositions, but recently Ritter *et al.*[20] reported the magnetic structure of Tb_5Ge_4 (the room-temperature crystal structure of the latter is essentially the same as that of Gd_5Ge_4). Indeed, in the 3D antiferromagnetic structure of Tb_5Ge_4, which is observed below 85 K in zero magnetic field, the individual slabs exhibit canted 2D ferromagnetism with the majority of Tb magnetic moments located within the slab, while the alignment of the magnetic moments of Tb in the neighboring slabs is antiparallel. It is therefore reasonable to predict that unusual magnetic phase transformations might be observed in Gd_5Ge_4 when the magnetic field and temperature vary. To date, the magnetic ground state of Gd_5Ge_4 in zero magnetic field has been assumed as that of a simple ferromagnet with a Néel temperature of ~15 K, as was reported earlier in Ref. 21.

Here we report on the magnetism of Gd_5Ge_4 prepared from high-purity components, which reveals the existence of both irreversible (below ~10 K) AFM→FM (antiferromagnetic→ferromagnetic) and reversible (above ~20 K) AFM↔FM magnetic phase transformations induced by the magnetic field when it exceeds certain critical value (H_{cr}). The critical magnetic field is a function of the temperature both below 10 K and above 20 K, but it becomes nearly temperature independent between 10 and 20 K. Furthermore, both the ferromagnetic and antiferromagnetic Gd_5Ge_4 phases were found to coexist during isothermal magnetization and demagnetization between 10 and 20 K, and below 10 K after cooling in magnetic fields ranging from 10 to 16 kOe. The ratio between the volume fractions of the two magnetically ordered phases in the chemically homogeneous specimen varies with the magnetic field at constant temperature. We also found that after the application of the magnetic field slightly lower than H_{cr} at 4.3 K, the irreversible AFM →FM transformation becomes unusually sluggish and it may continue for months.

II. EXPERIMENTAL DETAILS

The Gd_5Ge_4 compound was prepared by arc melting a stoichiometric mixture of the constituent elements using Gd (99.9 at. % purity) and Ge (99.99 at. % purity). Gadolinium was prepared by the Materials Preparation Center, Ames Laboratory, and contained the following major impurities (in ppm atomic): O-440; C-200; H-160; N-90; Fe-40; and F-30. Germanium was purchased from CERAC, Inc. The alloy (total weight ~15 g) was arc melted six times, with the button being turned over each time to ensure alloy homogeneity. Weight losses during arc melting were negligible and, therefore, the alloy composition was assumed to remain unchanged. No impurity phases were detected by x-ray powder diffraction and optical metallography of the as-cast Gd_5Ge_4 sample. The lattice parameters of our Gd_5Ge_4 sample were $a=7.6968(5)$, $b=14.831(1)$, and $c=7.7851(5)$ Å (see Ref. 19). Polycrystalline samples for the magnetization measurements weighted ~0.2 g. Based on the shape of the samples we estimate the demagnetization factor to be on the order of 0.3. Measurements of the magnetization were carried out using a Lake Shore, Model 7225 magnetometer in dc magnetic fields from 0 to 50 kOe. The rate of temperature change was ~1.5 K/min for both cooling and heating. The errors of magnetic measurements were about 1%.

III. RESULTS AND DISCUSSION

The magnetization of the zero-magnetic-field-cooled Gd_5Ge_4, measured in the isothermal regime in the temperature range between 4.3 and ~18 K, is shown in Fig. 1. At each temperature the magnetic field was cycled several times between 0 and 50 kOe. During the first magnetic field increase, at 4.3 K the magnetization in fields lower than ~18 kOe increases nearly linearly with the magnetic field and then exhibits a sharp discontinuity at $H_{cr}\approx 19$ kOe [Fig. 1(a)], indicating the appearance of a FM structure. The character of the transformation into the FM state observed in

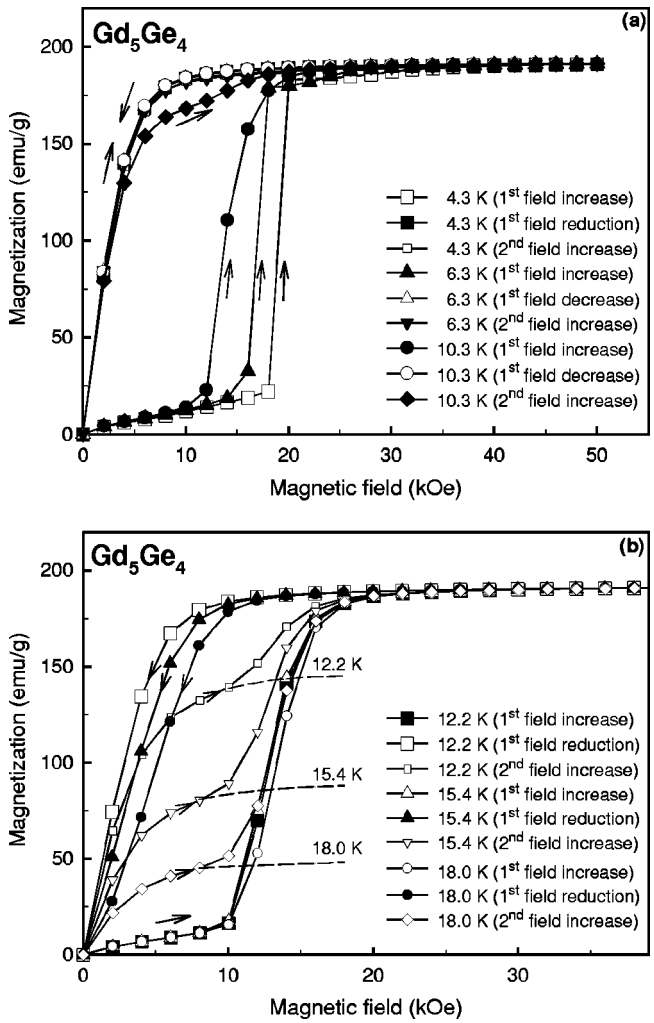

FIG. 1. The isothermal magnetization of Gd_5Ge_4 at 4.3, 6.3, and 10.3 K (a) and 12.2, 15.4, and 18.0 K (b). The expected behavior of the magnetization without the magnetic-field-induced AFM→FM transition is shown in (b) by the dashed lines.

Gd_5Ge_4 during the first application of the magnetic field is typical of a metamagnetic transition for the anisotropic Ising-type antiferromagnet.[22] During the second application of a magnetic field, the magnetization follows the first demagnetization path, showing that the entire sample remains in the FM state. Once formed, the ferromagnetic Gd_5Ge_4 phase is stable at 4.3 K after removal of the magnetic field, which was verified by holding the sample at 4.3 K in the zero magnetic field for ~12 h after initial magnetizing and demagnetizing. The magnetization vs magnetic field behavior measured after 12 h was the same as during the immediate second field application. In the ferromagnetic state the magnetization of Gd_5Ge_4 is typical for a soft ferromagnet with a coercivity of ~11 Oe, a remanence of ~0.5 emu/g, and a magnetic moment of $7.32\mu_B$/Gd atom in the saturated state at 4.3 K indicating a nearly collinear ferromagnetism. Zero-magnetic-field-cooled Gd_5Ge_4 appears to be antiferromagnetic (see below) and, therefore, the metamagnetic phase transition at 4.3 K is irreversible similar to that observed in the FeRh-based alloys (see, for example, Ref. 23). However,

as far as we are aware, no such behavior has been reported for $4f$-electron systems.

Above 4.3 K and below 10 K the value of H_{cr} decreases with temperature [Fig. 1(a)], while between ~10 and ~20 K the critical magnetic field becomes nearly constant and the metamagneticlike transition begins at ~11 and ends at ~18 kOe [Fig. 1(b)]. However, the magnetization during the second application of the magnetic field in this temperature range shows a much more complex behavior when compared to that below 10 K. Clearly, a ferromagneticlike behavior is observed from 0 to ~10 kOe, and it is followed by a steplike increase (i.e., a metamagneticlike transition) above 10 kOe. The value of the saturated magnetization in a 10-kOe magnetic field strongly depends on temperature, as shown in Fig. 1(b) by dashed lines, which represent the extrapolated behavior of the magnetization without the second step. We note that during the third and any additional application of a magnetic field between ~4.3 and ~20 K, the magnetization follows the same path as during the second field increase.

Between ~10 and 20 K the saturation magnetization during the first magnetic-field application is nearly constant, but the first saturation value of the magnetization during the second magnetic-field application (dashed lines) decreases with the increasing temperature; see Fig. 1(b). Based on this observation it is possible to conclude that in this temperature range the first application of the magnetic field induces the ferromagnetic state in the entire volume of the antiferromagnetic Gd_5Ge_4. When the magnetic field is removed, a fraction of the specimen volume is converted back to an antiferromagnetic state. Hence both the irreversible AFM→FM and reversible AFM↔FM transformations exist in Gd_5Ge_4 from ~10 to 20 K. The fraction of the Gd_5Ge_4 sample, which undergoes the reversible AFM→FM transformation, increases with temperature. At temperatures exceeding 20 K the magnetic-field-induced AFM↔FM transition becomes fully reversible, similar to that observed in $Gd_5(Si_{0.4}Ge_{3.6})$.[18]

Figure 2 illustrates the temperature dependencies of the dc magnetization of Gd_5Ge_4 in various dc magnetic fields measured during both the heating of a zero-magnetic-field-cooled sample and during cooling in a magnetic field. All of them show an anomaly around 130 K, which slightly shifts toward lower temperatures with increasing magnetic field (the positions of the anomaly are indicated by arrows in Fig. 2 and in the inset). Both the anomaly and its behavior as a function of magnetic field are typical of a phase transition between paramagnetic and antiferromagnetic states. Above ~200 K, $[\chi_{dc}(T)]^{-1}$ follows a Curie-Weiss law with a paramagnetic Curie temperature of 94 K and an effective magnetic moment of $(7.45\pm0.05)\mu_B$/Gd atom. Based on this evidence we classify Gd_5Ge_4 as an antiferromagnet with a Néel temperature of ~130 K, although the large positive Curie temperature points to a ferromagnetic ground state of this germanide. This is unusual because the AFM ordering observed in Gd_5Ge_4 at ~130 K is a clear indication that negative exchange, i.e., antiferromagnetic interactions, are dominant. Therefore, it appears that both positive and negative exchange interactions play a role in the formation of the long-range magnetic order of Gd_5Ge_4, which agrees with the model of the magnetic structure suggested by Ritter *et al.*[20]

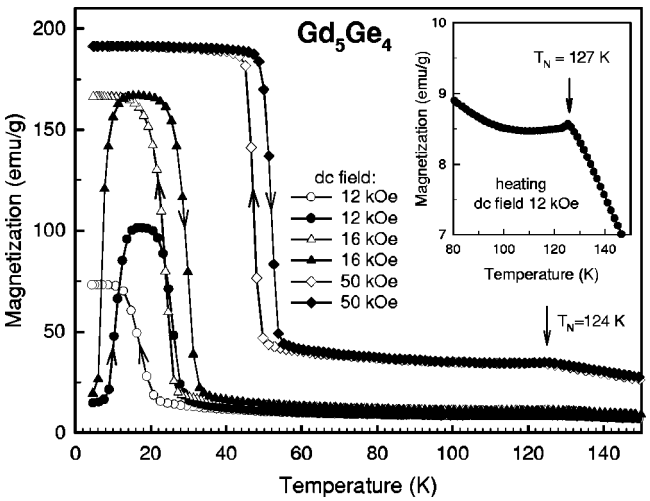

FIG. 2. Temperature dependencies of the magnetization of Gd_5Ge_4 measured in dc magnetic fields between 12 and 50 kOe during heating (filled symbols) and cooling (opened symbols). Before measurements were made on heating, the sample was cooled to the lowest temperature of the measurement in a zero magnetic field. The inset shows an expanded view of the magnetization between 80 and 150 K in the 12-kOe magnetic field.

for Tb_5Ge_4 (where intra slab ferromagnetism is coupled to the antiferromagnetic arrangement of the slabs).

On heating in magnetic fields below ~16 kOe, the magnetization of the zero-magnetic-field-cooled Gd_5Ge_4 shows a broad, plateaulike anomaly centered at ~19 K, and both its magnitude and width increase with the magnetic field (see Fig. 2). This behavior correlates with the presence of both the low-temperature AFM→FM and high-temperature FM →AFM transitions in the sample, and shows that the ferromagnetic state in the zero-field-cooled Gd_5Ge_4 exists only in a narrow temperature range, e.g., between ~6 and 34 K in the 16-kOe magnetic field. Furthermore, on heating from ~4 K in the 16-kOe magnetic field, the magnetization of Gd_5Ge_4 shows a tremendous change from ~20 to ~170 emu/g when the temperature increases only by ~3 K (Fig. 2), reflecting that the parameters of the AFM→FM transition depend strongly on the thermal excitation of the lattice. In magnetic fields exceeding ~20 kOe at 4.3 K, Gd_5Ge_4 is already transformed into a FM state. Hence the temperature dependence of the magnetization reflects only one FM→AFM transition, and its temperature increases with magnetic field at a rate of ~0.8 K/kOe.

On cooling, the magnetization of Gd_5Ge_4 changes similarly to that observed on heating in magnetic fields exceeding 20 kOe, and exhibits a thermal hysteresis of ~6 K in the vicinity of the AFM↔FM phase transition (e.g., see the 50-kOe magnetization vs temperature in Fig. 2). When cooled in magnetic fields between 8 and 20 kOe, Gd_5Ge_4 transforms only partially into the ferromagnetic state. Figure 3 shows the isothermal magnetization of Gd_5Ge_4 measured at 4.3 K after cooling it in various dc magnetic fields (the cooling rates were ~1.5 K/min). The amount of the FM phase formed increases from 0 ($H_{dc}\leqslant 8$ kOe) to ~35% ($H_{dc}=12$ kOe), ~70% ($H_{dc}=14$ kOe), and 100% (H_{dc}

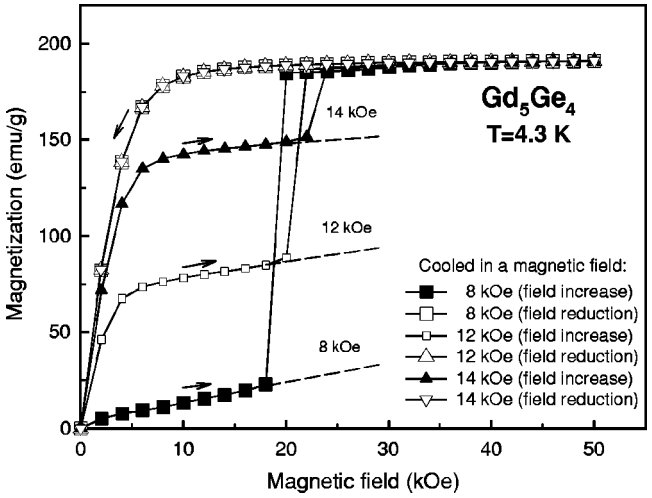

FIG. 3. The magnetization of Gd_5Ge_4 measured in the isothermal regime at 4.3 K after the sample was cooled in different dc magnetic fields.

$\geqslant$20 kOe) showing that the extent of the AFM$\rightarrow$FM transition is easily controlled by the magnitude of the magnetic field during cooling. We note that H_{cr} increases with the fraction of the formed ferromagnetic phase (Fig. 3), which can be explained by stress build up due to different volumes of the AFM and FM phases assuming that a crystallographic transition occurs together with the ferromagnetic ordering similarly to that found in the $Gd_5(Si_{0.4}Ge_{3.6})$ alloy.[18]

Finally, an unusual phenomenon of a time-dependent magnetization in Gd_5Ge_4 is observed when the sample is placed in a dc magnetic just below the critical value of 18 kOe. This is shown in Fig. 4 as the time dependence of the magnetization at 4.3 K of the zero-magnetic-field-cooled Gd_5Ge_4 in the 17-kOe magnetic field. As one can see, the

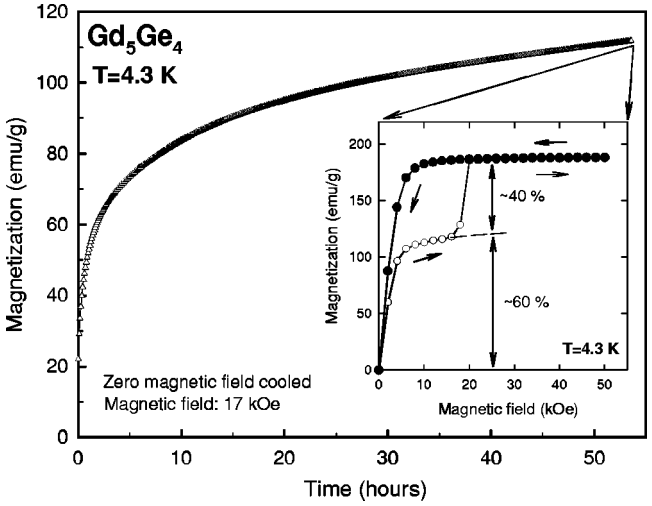

FIG. 4. Time dependence of the magnetization of zero-magnetic-field-cooled Gd_5Ge_4 at 4.3 K in a 17-kOe magnetic field. The inset shows the magnetization of Gd_5Ge_4 measured after the sample was held for 54 h in the 17-kOe magnetic field. The magnetic field was reduced to zero before the measurement of the magnetization isotherm without changing the temperature of the sample.

isothermal magnetization of Gd_5Ge_4 continues to rise even after 50 h. The inset of Fig. 4 is the full magnetization isotherm of Gd_5Ge_4 measured at 4.3 K immediately after terminating the magnetization vs time measurements. The ratio between the saturation magnetization before and after the magnetic-field-induced transformation observed during the first application of the magnetic field shows that $\sim$60% of the sample volume has been transformed from the AFM into the FM state isothermally during $\sim$54 h in the 17-kOe magnetic field, and $\sim$40% of the sample volume remains in the AFM state. Both the AFM and FM phases coexist in Gd_5Ge_4 during this transformation, thus creating a magnetically heterogeneous system in a chemically homogeneous specimen. The fraction of the FM phase in the AFM matrix shows a nearly logarithmic time dependence, indicating that at this magnetic field and temperature the completion of the AFM $\rightarrow$FM transition will occur in $\sim$18 months. To the best of our knowledge this is the first observation of such an abnormally sluggish magnetic phase transformation induced by an undercritical magnetic field in an isothermal regime. At this time we can only speculate that this unusual magnetic phase transformation kinetics is closely related to the simultaneous phase volume change, which is nearly 1.5% when the transformation is completed.

Based on our experimental data it is clear that the magnetic phase transitions in Gd_5Ge_4 below $\sim$10 K and above $\sim$20 K are different in nature, even though in both cases the application of a magnetic field at or above H_{cr} is required to overcome the energy barrier between AFM and FM phases under isothermal conditions. Below 10 K the critical magnetic field increases with lowering the temperature because thermal fluctuations of the localized magnetic moments and/or elasticity of the lattice in the AFM state are reduced, thus enhancing negative exchange interaction. Hence the increased negative exchange interaction raises both the free-energy difference between the AFM and FM phases, and the critical magnetic field required to accomplish the transition. Assuming that the formation of the FM phase in Gd_5Ge_4 is accompanied by a change of the crystal structure, this results in the dominating positive exchange interaction and thermal fluctuations at low temperature not being strong enough to destroy the ferromagnetic state induced in Gd_5Ge_4. The AFM$\rightarrow$FM transition, therefore, is irreversible below $\sim$10 K. On the other hand, the free-energy difference between AFM and FM phases also increases with temperature above 20 K, and so does the critical magnetic field, similar to what is observed in all $Gd_5(Si_xGe_{4-x})$ alloys when $x \leqslant 2$.[15] This increase may be associated (1) with the increased thermal fluctuations, which require larger magnetic work to overcome the rising thermal energy of the lattice; (2) with the unusual thermal expansion of the Gd_5Ge_4 crystal lattice, where the small changes in interatomic distances may have a pronounced effect on the free energies of both the antiferromagnetic and ferromagnetic states; or (3) with both. The reversibility of the phase transformation above 20 K is likely caused by the increased thermal energy of the lattice and by the large difference in the free energy of the two different magnetic (and crystallographic) states of the Gd_5Ge_4 system.

IV. CONCLUSIONS

Hence Gd_5Ge_4 shows quite unexpected magnetic correlations that are sensitive to the magnitude of the applied dc magnetic field, temperature, and directions of their change. Taking into account the specific layered crystal structure of Gd_5Ge_4, we conclude that a rich variety of the observed magnetic transformations is brought about by the strongly anisotropic exchange interactions. We believe that within the slabs positive exchange dominates, thus resulting in a nearly collinear two-dimensional ferromagnetism. However, exchange interactions between the slabs are negative, which results in an antiferromagnetic ground state of Gd_5Ge_4 in a zero magnetic field. Application of the magnetic field at or above certain critical value, which varies with temperature, transforms the antiferromagnetic Gd_5Ge_4 into a three-dimensional ferromagnetic system. Our conclusions are in accord with the recent experimental data on the magnetic structure of the closely related Tb_5Ge_4 system reported by Ritter *et al.*,[20] and with the recent theoretical model proposed by Rotter *et al.*[24] which showed that anisotropic exchange interactions may be responsible for the formation of noncollinear amplitude modulated structures in Gd-based materials, and that in this case the magnetic structure could be extremely sensitive to small details of this exchange.

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