Interplay between reversible and irreversible magnetic phase transitions in polycrystalline Gd_5Ge_4

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Temperature and magnetic field dependent magnetization and heat capacity of polycrystalline Gd_5Ge_4 have been measured. In addition to the antiferromagnetic ordering observed at the Néel temperature, $T_N = 128$ K, there is a cusp at ~ 17.5 K in the low-field zero-field cooled (zfc) $M(T)$ curves, below which the zfc and field-cooled (fc) magnetic data exhibit irreversibility. The zfc and fc magnetization data show a complex mixture of reversible and irreversible behaviors at fields between ~ 10 and ~ 18 kOe, which is correlated to the magnetic field induced transitions between the antiferromagnetic (*AFM*) and the ferromagnetic (*FM*) states. The initial zfc $M(H)$ data below a certain temperature exhibit two transitions: a discontinuous metamagnetic-like transition and a continuous magnetic moment rotation process. The anomalies in the isofield and isothermal magnetization data indicate a complex magnetic structure at low temperatures, e.g., a complex canted *AFM* structure. In addition, magnetic field or temperature induced $AFM \leftrightarrow FM$ transitions occur under certain conditions. The unusual magnetic behavior is discussed in terms of a possible complex magnetic structure at low temperatures and a martensitic-like structural change induced by the magnetic field

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INTRODUCTION

The $Gd_5(Si_xGe_{1-x})_4$ alloys display unusually potent magnetocaloric,[1,2] magnetostrictive,[3,4] and magnetoresistance[5–7] effects when $x \leqslant \sim 0.5$. All are believed to be associated with a first-order magnetic phase transition accompanying the simultaneous occurrence of a martensitic-like structural change. As a result, the latter can be induced by varying the magnetic field and/or by changing the temperature. Unlike other members of the series, Gd_5Ge_4 appears to remain antiferromagnetic (*AFM*) in zero field between ~ 2 and 130 K, and the magneto-structural transformation in the germanide can only occur in the presence of magnetic field exceeding 10 kOe.[8–10]

Certain aspects of the magnetic, elastic, and electrical properties, and electronic structure of Gd_5Ge_4, which is one of the end compounds in the pseudo-binary $Gd_5(Si_xGe_{1-x})_4$ system, have been addressed recently.[8–11] Gd_5Ge_4 has the complex Sm_5Ge_4-type orthorhombic structure at room temperature,[11] and it shows some peculiar magnetic features at low temperatures, for example, the magnetic field induced antiferromagnetic (*AFM*) to ferromagnetic (*FM*) and the subsequent temperature induced $FM \leftrightarrow AFM$ transitions.[9] In addition, it has been shown that upon dilution with Si, $Gd_5(Si_xGe_{1-x})_4$ with $x = 0.1$ (an alloy which is isostructural with Gd_5Ge_4 at room temperature) exhibits a martensitic-like structural change coupled with the $AFM \leftrightarrow FM$ transition at low temperature in zero magnetic field.[3] Therefore, it is reasonable to assume that there may be a similar martensitic-like crystallographic change in the pure germanide, and as a result, there may be some change in the magnetic behaviors related to the structural distortion. As shown recently by Magen *et al.*,[10] a structural change in Gd_5Ge_4 occurs in the presence of a magnetic field. Its atomic scale mechanism has been established by Pecharsky *et al.*[12]

Although the preliminary magnetic field (H)-temperature (T) magnetic phase diagram has been determined for Gd_5Ge_4,[8] some features, including the thermal irreversibility of magnetic properties at low temperatures in magnetic fields less than 20 kOe; the two-component contributions to the magnetization process in the zero field cooled (zfc) initial $M(H)$ curves; and magnetic hysteresis in fields below 20 kOe and at temperatures below 20 K have not been addressed in detail. The underlying mechanisms of these anomalies, therefore, have not been yet elucidated. The mentioned anomalous phenomena are likely related to a complex magnetic structure of the material at low temperatures, e.g., a canted antiferromagnet, assuming that it may be similar to that reported in the Tb_5Ge_4 compound.[13,14]

In this work, we present the results of an investigation of the thermal irreversibility and magnetic hysteresis at low temperature, and propose our understanding of the phenomena based on assumptions that (1) a complex magnetic structure exists at low temperatures, and (2) that Gd_5Ge_4 undergoes a martensitic-like crystallographic phase change simultaneously with a *FM* ordering transition under certain conditions. The H-T magnetic phase diagram of the titled compound was refined taking into account both the reversible and irreversible nature of the $AFM \leftrightarrow FM$ transitions induced by magnetic field and/or temperature.

EXPERIMENTAL DETAILS

The polycrystalline Gd_5Ge_4 sample was prepared by arc melting the stoichiometric mixture of constituent elements Gd (99.9 at. % purity) and Ge (99.999 at. % purity). The Gd was prepared by the Materials Preparation Center at the Ames Laboratory, and contained the following major impurities (in ppm atomic): O-440, C-200, H-160, N-90, Fe-40, and F-30. The Ge was purchased from Meldform Metals. The as-cast Gd_5Ge_4 was characterized by x-ray powder diffraction and optical metallography, and was found to be a single-phase material with the Sm_5Ge_4-type orthorhombic structure at room temperature.[11] The magnetization measurements were carried out in a LakeShore magnetometer/susceptometer (model 7225). The zero-field cooled (zfc) isothermal magnetization, $M(H)$, was measured after cooling the Gd_5Ge_4 sample from ~180 K (~50 K higher than the observed $PM \leftrightarrow AFM$ transition temperature) to 4.2 K in zero magnetic field and then warming up to the desired temperature in zero magnetic field. The zfc isofield magnetization, $M(T)$, was measured at the desired magnetic field during heating with a rate of 1.5 K/min. The field cooled (fc) $M(T)$ behaviors were measured at the specific magnetic fields during heating after cooling the sample from ~180 to 4.2 K in the same magnetic field. Some $M(H)$ data were also collected at selected temperatures after measuring the initial zfc $M(H)$ behavior at 4.5 K and then warming up to the desired temperature in zero magnetic field, in order to verify both the magnetic state of the Gd_5Ge_4 compound after it was previously magnetized at a lower temperature and the reversibility of the magnetic field induced phase transition in this compound. In addition, the heat capacity data were collected on heating in an automatic semi-adiabatic heat pulse calorimeter[15] at various magnetic fields after cooling the sample in zero magnetic field.

EXPERIMENTAL RESULTS

Zero field cooled and field cooled $M(T)$ data and irreversibility

The zfc and fc $M(T)$ behavior of Gd_5Ge_4 are shown together in Fig. 1 (in magnetic fields of 10 kOe and below), in Fig. 2 (in magnetic fields between ~12 and 16 kOe), and in Fig. 3 (in magnetic fields above 20 kOe). In all magnetic fields, there is a weak anomaly at ~128 K, which can be attributed to the $AFM \leftrightarrow PM$ magnetic phase transition as has been well documented in the literature,[8–11,16] and illustrated in the inset in Fig. 1. In the case of magnetic fields of 10 kOe and below, there is a cusp with a maximum at ~17.5 K, in both the zfc and fc $M(T)$ curves. Below ~17.5 K, the zfc and fc $M(T)$ branches diverge, and above this temperature the zfc and fc $M(T)$ data are identical. Measurements of the ac magnetic susceptibility as a function of temperature indicate that the cusp shows no frequency dependence, thus ruling out the possibility of magnetic disorder, i.e., a spin glass with T_f around 17.5 K. Both the cusp at ~17.5 K and the irreversibility below 17.5 K cannot be attributed to the AFM transition occurring at ~128 K (zero field). The two arguments are as follows: First, the corresponding $AFM \rightarrow PM$ transition temperature is ~128 K (zero field, heating process) and the thermal divergence between the zfc and fc $M(T)$ curves should be observed just below 128 K in low magnetic fields. Second, initial zfc $M(H)$ data, that will be presented later, show that no magnetic transitions occur at fields below 10 kOe.

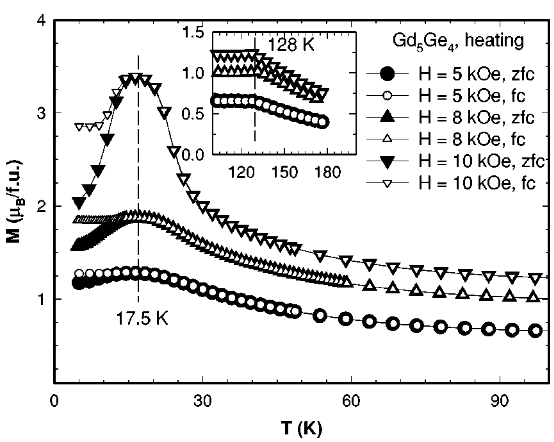

FIG. 1. The zfc and fc $M(T)$ data for polycrystalline Gd_5Ge_4 measured in low magnetic fields during heating.

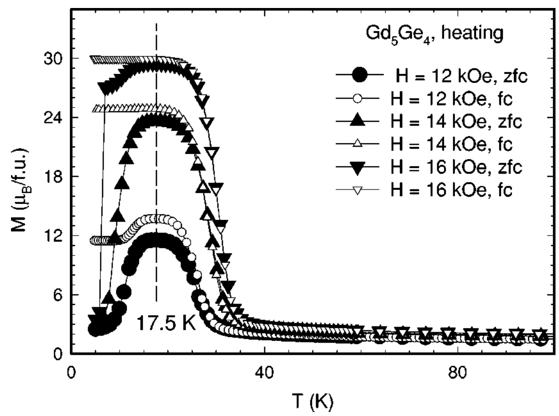

FIG. 2. The zfc and fc $M(T)$ data for polycrystalline Gd_5Ge_4 measured in intermediate magnetic fields during heating.

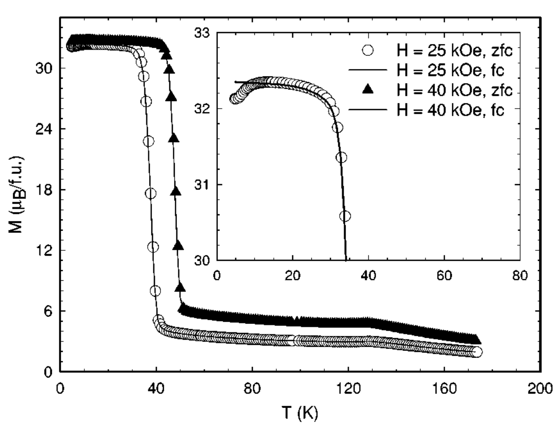

FIG. 3. The zfc and fc $M(T)$ data for polycrystalline Gd_5Ge_4 measured at 25 and 40 kOe during heating. The inset clarifies the behavior at the lowest temperature for $H = 25$ kOe.

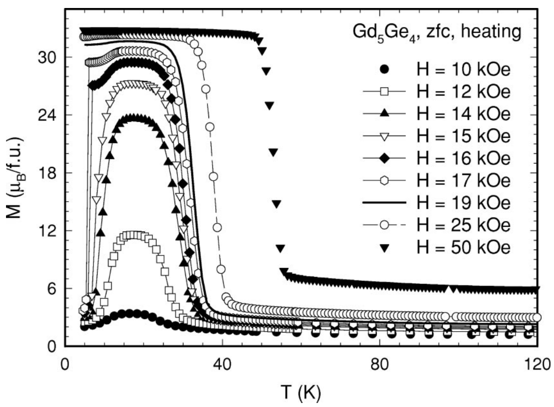

FIG. 4. The zfc magnetization of polycrystalline Gd_5Ge_4 as a function of temperature at various dc magnetic fields, measured during heating.

As shown in Fig. 2, in the magnetic field range from ~12 to 16 kOe, the zfc and fc $M(T)$ data display different features. Compared to the cases with applied fields lower than 10 kOe (Fig. 1), the maximum magnetization value in each curve increases sharply in magnitude in this range of magnetic field. It is obvious that there are basically two types of transitions (from *AFM* to *FM*, and then from *FM* to *AFM* on heating) at low temperatures, besides the $AFM \rightarrow PM$ transition occurring at ~128 K.[8,9,11,16] The $AFM \rightarrow FM$ transition at the lowest temperature has also been verified by the initial zfc $M(H)$ data (will be shown in the following section). The irreversibility between the zfc and fc $M(T)$ curves is maintained on heating up to the corresponding $FM \rightarrow AFM$ transition, the temperature of which increases with increasing magnetic field. This behavior is different from the features observed at fields below 10 kOe (Fig. 1), where the irreversibility disappears at a constant temperature coinciding with the cusp at ~17.5 K on heating. The cusp observed around 17.5 K in zfc $M(T)$ data is no longer seen in fc $M(T)$ data when the applied magnetic field equals to or exceeds 14 kOe. The changes in the irreversibility with respect to magnetic field are associated with the temperature-induced $AFM \rightarrow FM$ transition during field cooling in the magnetic field above 10 kOe and the appearance of a mixture of the *AFM* and *FM* states in the temperature range from ~8 to ~22 K after field-cooling the sample, as will be shown in the next section. For the cases with magnetic field between 16 and 18 kOe, the zfc $M(T)$ branches (also see Fig. 4, below) show a discontinuity at low temperature, which is dependent upon the applied magnetic field, indicating that there is a metamagnetic $AFM \rightarrow FM$ transition triggered at a specific magnetic field by varying temperature.

The zfc and fc $M(T)$ data above 20 kOe exhibit features different from those observed in low and medium magnetic fields, as shown in Fig. 3 for 25 and 40 kOe as typical zfc and fc $M(T)$ behaviors. At low temperatures, the compound is basically in the *FM* state when the magnetic field exceeds 19 kOe, except for a subtle structure still observed at the lowest temperature in the zfc $M(T)$ curves below ~10 K, as shown in the inset of Fig. 3 for a magnetic field of 25 kOe. Recent x-ray diffraction studies[12] also revealed structural transitions induced by application/removal of a magnetic field at low temperatures, i.e., the transition between the Gd_5Si_4-type and the Sm_5Ge_4-type orthorhombic structures induced by magnetic field under certain conditions. The likely origin of this low temperature anomaly in the zfc magnetization data may be the temperature dependence of imperfectly collinear configuration of magnetic moments at the lowest temperatures. However, we cannot exclude the possibility of a dynamical process associated with the relaxation of the magnetic field induced $AFM \rightarrow FM$ transformation, which was noted in the dynamic measurements near the critical magnetic field.[9] The zfc and fc $M(T)$ branches become identical to one another above ~10 K in 25 kOe and at all temperatures in a 40 kOe magnetic field or above.

In order to illustrate the gradual change in $M(T)$ in various magnetic fields and the underlying magnetic phase transitions and/or magnetic structure changes with temperature, we show in Fig. 4 the zfc $M(T)$ data of the thermally demagnetized Gd_5Ge_4 sample measured from ~4.5 to ~180 K on heating in various magnetic fields. Not shown here is the transition at ~128 K (when $H=0$ kOe) which is slightly shifted towards lower temperature with increasing magnetic field, i.e., it occurs at ~126 K in 50 kOe. The low temperature portions of the zfc $M(T)$ data display a bell-like anomaly in low magnetic fields, which gradually increases in the amplitude with rising field in the range from 10 to 15 kOe. The low temperature side of the anomaly indicates $AFM \rightarrow FM$ transition, and its high temperature side corresponds to $FM \rightarrow AFM$ transition. Bell-like anomalies are centered at ~17.5 K in magnetic fields below 15 kOe, but a plateau around this temperature develops and gradually broadens as magnetic field increases beyond 15 kOe. When the magnetic field reaches 16–18 kOe, the nearly symmetric bell-like anomaly in the zfc $M(T)$ curves evolves into a discontinuity on the low temperature side, followed by a gradual increase in the amplitude plus a plateau, while the high temperature side remains continuous in all magnetic fields. The discontinuity signals a metamagnetic transition induced by temperature variation at magnetic fields of 16 and 17 kOe.

To summarize the data presented in Figs. 1–4, the zfc $M(T)$ behaviors in magnetic fields less than ~10 kOe suggest a re-arrangement of a complex *AFM* structure induced by heating, which is manifested by a broad peak at ~17.5 K. The zfc $M(T)$ data in magnetic fields between ~10 and ~19 kOe point to a different picture, i.e., upon heating there is an $AFM \rightarrow FM$ transition followed by a $FM \rightarrow AFM$ magnetic phase transition in a constant magnetic field. The zfc $M(T)$ data measured in fixed magnetic fields larger than 19 kOe reveal a magnetic phase transition from *FM* to *AFM* upon heating at temperatures between ~25 and ~55 K. In addition, for $H>19$ kOe a subtle feature below ~10 K, which may be associated with the temperature dependence of the nearly collinear spin structure or with the time dependent magnetization at the lowest temperatures in fields up to 35 kOe, is observed. Some thermal divergence between the zfc and fc $M(T)$ data is noted below ~35 kOe, which disappears in higher magnetic fields.

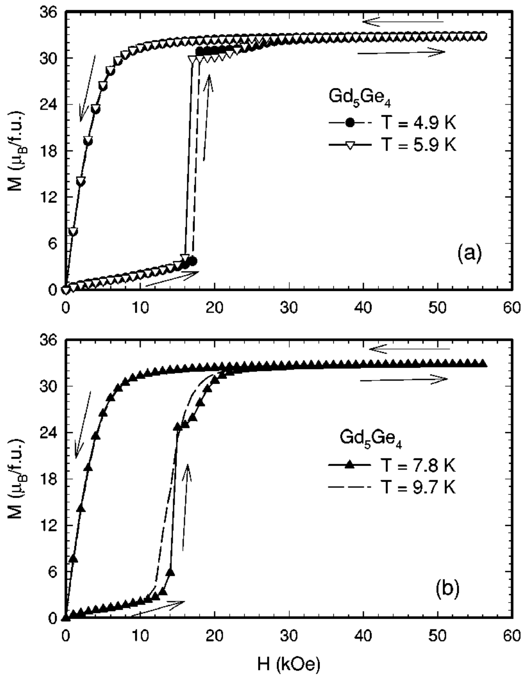

FIG. 5. Initial magnetization and the field-decreasing branches measured at 4.9 and 5.9 K (a), and 7.8 and 9.7 K (b). The data were taken after zero-field cooling from 180 to 4.2 K and then warming up to the temperatures of measurement in zero field. The arrows indicate the magnetic field change direction.

ISOTHERMAL MAGNETIZATION, *M(H)*

In order to clarify the magnetic states at different temperatures and fields, we carried out measurements of the isothermal magnetization under various conditions. The initial magnetization data and the corresponding field-decreasing branches at different temperatures are shown in Figs. 5–7. Each curve was obtained by measuring the polycrystalline Gd_5Ge_4 sample in the virgin state after zero-field cooling from the paramagnetic region. Figure 5 shows the data at temperatures between 4.9 and ~10 K, Fig. 6 is for the cases

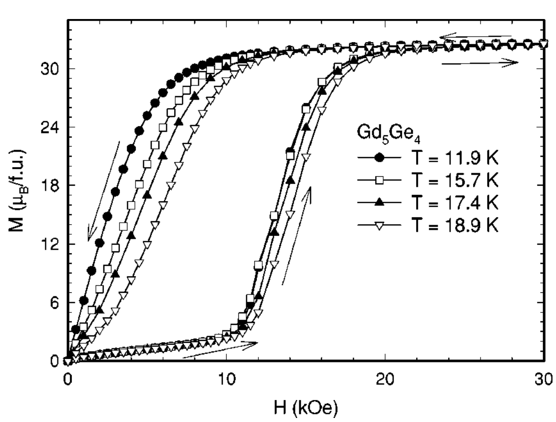

FIG. 6. Initial magnetization and the field-decreasing branches measured between 10 and 20 K. The data were taken after zero-field cooling from 180 to 4.2 K and then warming up to the temperatures of measurement in zero field. The arrows indicate the magnetic field change direction.

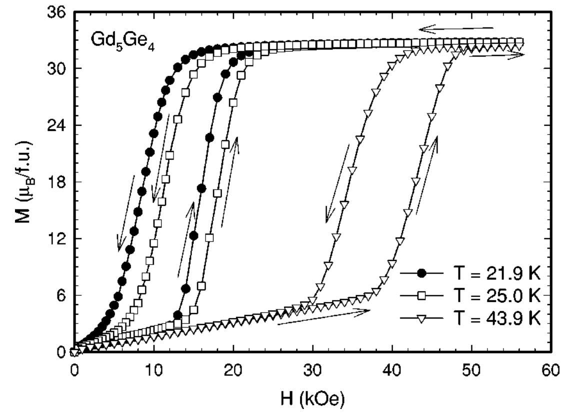

FIG. 7. Initial magnetization and the field-decreasing branches measured above 20 K. The data were taken after zero-field cooling from 180 to 4.2 K and then warming up to the temperatures of measurement in zero field. The arrows indicate the magnetic field change direction.

with temperature from ~12 to ~19 K, and Fig. 7 represents magnetization measured at temperatures between ~22 and 45 K. Above ~50 K, no magnetic field-induced transitions have been observed in the initial $M(H)$ data in the magnetic field below 56 kOe. Comparing these three figures, it is obvious that the magnetization behavior is different in each of the three ranges of temperature. Below ~8 K, as shown in Fig. 5, a discontinuous metamagnetic transition occurs, with a critical magnetic field decreasing from ~18 kOe at 4.5 K to ~14 kOe at ~8.0 K. Furthermore, two components in $M(H)$ curves are clearly seen during the transition from *AFM* to *FM* state in this temperature range. A possible model for these behaviors is as follows: A sharp discontinuity, which may be due to a metamagnetic transition, followed by a continuous moment rotation process, i.e., the further alignment of spins with increasing magnetic field beyond the critical value. These two kinds of events are schematically shown in Fig. 8, as a discontinuous metamagnetization process

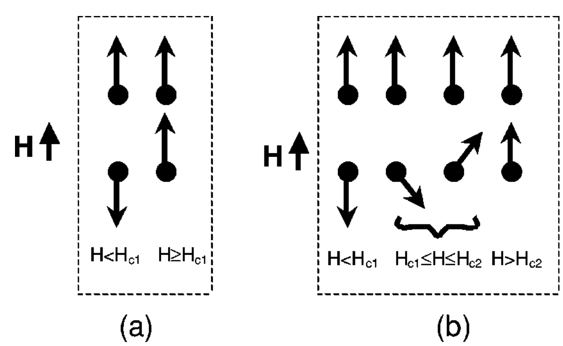

FIG. 8. The schematic diagram of the two types of the magnetization process in an *AFM* system: (a) The discontinuous metamagnetic transition, and (b) the continuous rotation of magnetic moments. In the former case, there exists only one critical magnetic field, but there are two critical magnetic field values in the latter case and the transition begins at a field above H_{c1} and ends at a magnetic field above H_{c2}, between H_{c1} and H_{c2} there is a mixed state of field induced *FM* and *AFM* phases.

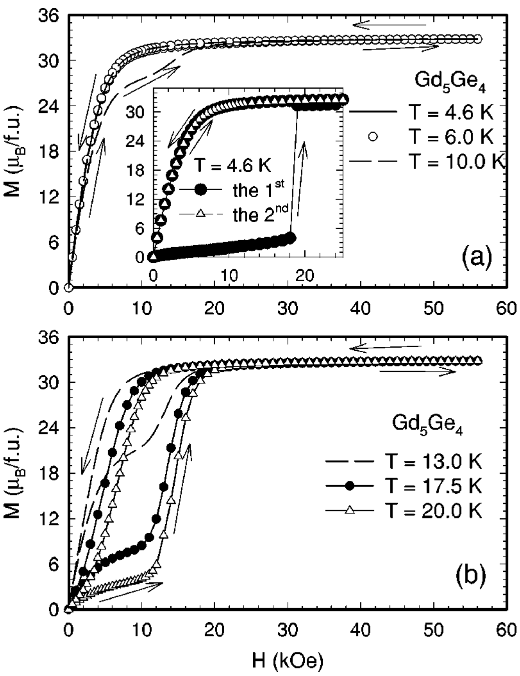

FIG. 9. Magnetization data $M(H)$ and the corresponding field-decreasing branches of polycrystalline Gd_5Ge_4 measured at various temperatures after the sample was magnetized at 4.5 K using a 56 kOe magnetic field and then warmed in zero magnetic field up to the measurement temperature: (a) Temperature between ~4.5 and ~10 K; (b) temperatures between ~13 and ~20 K. The arrows indicate the magnetic field change direction.

[Fig. 8(a)][17,18] and a continuous spin rotation [Fig. 8(b)],[17,19] respectively. In Gd_5Ge_4, for example, the latter component in the virgin $M(H)$ data persists from ~18 to ~35 kOe field at 4.9 K and from ~16 to ~24 kOe at 7.8 K. The relative contribution of these two components to the magnetization value changes systematically, i.e., the metamagnetic discontinuity becomes less evident and the continuous moment rotation becomes more prominent, and finally dominates with increasing temperature to ~9.7 K.

Assuming that the magnetic structure of Gd_5Ge_4 at low temperatures may be similar to that observed in Tb_5Ge_4,[13,14] a gradual transformation from metamagnetism to continuous moment rotation indicates a complex temperature dependence of the magnetic structure. Additionally, there is a distinct hysteresis between the field-increasing and field-decreasing branches of $M(H)$ data but with zero coercivity. After being magnetized and when the magnetic field is reduced to zero at a temperature below ~8 K, the system remains ferromagnetic indefinitely provided the temperature remains constant or remains below 8 K. This is easily derived from a second magnetization process following the first demagnetization branch, as seen in the inset of Fig. 9(a), thus confirming the irreversible nature of the $AFM \rightarrow FM$ magnetic phase transition in this temperature range.

As shown in Fig. 6, the magnetic field induced $AFM \rightarrow FM$ transition in the thermally demagnetized Gd_5Ge_4 sample has a nearly constant critical field value of ~10.5 kOe in the temperature range from ~12 to ~22 K. The $M(H)$ data in this temperature range exhibit a gradually increasing magnetization unlike the discontinuous behavior of $M(H)$ below ~10 K. The hysteresis existing between the field-increasing and the field-decreasing branches shows no coercivity and confirms the first-order nature of the magnetic field induced $AFM \rightarrow FM$ transition. At a temperature above ~12 K, the field-decreasing branch gradually deviates from the pure *FM* behavior and begins to display a step-behavior (see the low-field portion on the field-decreasing branches of Fig. 6), which indicates a mixture of *AFM* and *FM* states in this temperature range (~12–~22 K) upon the removal of the magnetic field. Therefore, the $AFM \leftrightarrow FM$ transitions in the temperature range of ~12–~22 K become partially reversible, as was concluded earlier.[9]

Above ~22 K, the magnetic field induced $AFM \rightarrow FM$ transition and the hysteresis between the $AFM \rightarrow FM$ transition and the reverse $FM \rightarrow AFM$ transition remain, but shift to higher magnetic field with increasing temperature. The $AFM \leftrightarrow FM$ transitions become completely reversible but with a hysteresis of ~10 kOe for each temperature in this range. Unlike the behavior observed below ~22 K, where the magnetization is dependent upon the previous magnetization history, the $M(H)$ behavior is completely repeatable for each temperature above ~22 K when magnetic field is cycled. Considering the irreversibility of the magnetic field induced transition below ~8 K, and its partial reversibility between ~8 and ~22 K, we conclude that the *AFM* state above ~22 K is different from that observed below ~8 K. In fact, the magnetic field induced $AFM \leftrightarrow FM$ transitions in Gd_5Ge_4 above ~22 K is quite similar to that of $AFM \leftrightarrow FM$ transformation reported in the $Gd_5Si_{0.4}Ge_{3.6}$ (Ref. 3) compound and the magnetic field induced $PM \leftrightarrow FM$ transitions reported in the $Gd_5Si_2Ge_2$ compound.[6,7] The critical fields corresponding to the $AFM \rightarrow FM$ transition increase with increasing temperature in this range, which is understandable by considering that the Gibbs free energy difference between the two states increases with increasing temperature and the transformation from one state to another requires a higher static magnetic energy ($\mu_0 MH$) to overcome the free energy difference.[20]

The magnetic field induced *FM* interactions arise from *AFM* state due to the sign reversal of the magnetic exchange parameter $\boldsymbol{J}_{ex}$. This sign reversal is likely related to the magnetic field induced structural change. In this compound, the *FM* interactions, which are induced by the application of magnetic field, are weak. Hence, the system can be transformed back to the *AFM* state by removal of the magnetic field at temperatures above ~22 K or by elevating temperature after the field has been removed. The complete or partial recovery of the *AFM* state from the field-induced *FM* state by the removal of magnetic field has been noted above by the corresponding field-decreasing branches in $M(H)$ data at temperatures above ~12 K (Figs. 6 and 7). To better understand the interplay between the *FM* and *AFM* states, we studied the temperature dependence of the *AFM* state recovered from the magnetic field induced *FM* state. Shown in Fig. 9 are the $M(H)$ curves measured at various temperatures after the thermally demagnetized sample was magnetized at 4.5 K using a 56 kOe magnetic field and then warmed up to the

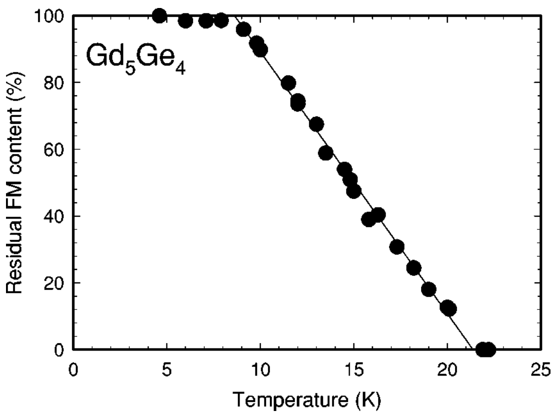

FIG. 10. Temperature dependence of the amount of the residual *FM* phase in the polycrystalline Gd_5Ge_4 sample after initial magnetization at 4.5 K. The *FM* content was evaluated from the $M(H)$ data at the individual temperatures by extrapolating the corresponding low magnetic field steps to the 56 kOe field and computing a ratio to the magnetization value of sample at 56 kOe field. The solid circles are the experimental data, the broken line is the guide for the eye, and the solid line is the least squares fit to the experimental data in the range of 9–21 K.

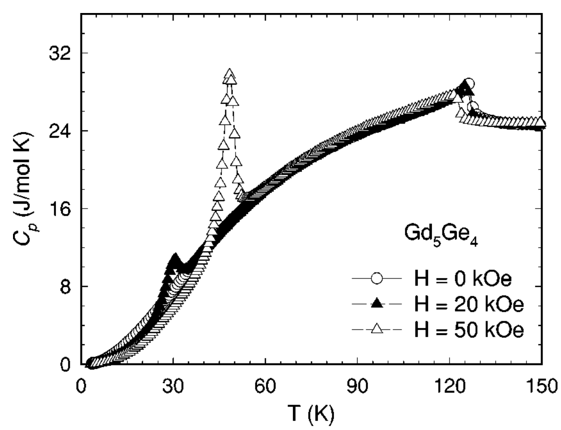

FIG. 11. The heat capacity of polycrystalline Gd_5Ge_4 as a function of temperature measured in magnetic fields of 0, 20, and 50 kOe after cooling the sample in zero field. The heat capacity data were taken on heating.

temperature of measurement in zero field. The lowest temperature data (4.6 K) in Fig. 9(a) confirm the previously reported results:[9] The induced *FM* state remains stable in zero magnetic field at this temperature. The sample remains ferromagnetic when warmed up to a temperature as high as 8 K in zero magnetic field. However, when the measurement temperature is increased to ~10 K or above, a distinguishable step-behavior in the $M(H)$ data indicates that a fraction of the field induced *FM* phase has been thermally transformed back to the *AFM* state. The amount of the remaining *FM* phase is dependent upon temperature and it decreases with increasing temperature in the range from 10 to 20 K, as clearly seen in Fig. 9(b) from the gradually decreasing amplitude of the first step in the $M(H)$ data.

Figure 10 shows quantitatively the temperature dependence of the residual *FM* phase in the Gd_5Ge_4 compound as a function of temperature after being initially magnetized at 4.5 K. The amount of the residual *FM* phase was evaluated from the $M(H)$ data by employing a method similar to that described by Levin *et al.*[9] Below ~8.6 K, the premagnetized Gd_5Ge_4 sample remains in the *FM* state. The *AFM* state is recovered from the magnetic field induced *FM* state in a linear fashion between ~8.6 and ~21.3 K, as indicated by the solid line in Fig. 10. The concentration of residual *FM* phase can be determined from $f(T)=100-7.9\times(T\text{-}8.6)$ between 8.6 and 21.3 K, where $f(T)$ is weight percent of the *FM* phase and T is temperature. This partial transformation process between *AFM* and *FM* is fully repeatable at each temperature in this range, regardless of the previous magnetization history. In other words, the second, the third and additional applications of the magnetic field at constant temperature follow the first magnetization and demagnetization path shown in Fig. 9. Therefore, as demonstrated in Fig. 10, the partially recovered *AFM* state exists in the temperature range from ~8.6 to ~21.3 K together with the residual *FM* state in the Gd_5Ge_4 sample which was premagnetized at a lower temperature. Above ~21.3 K, the *AFM* state is fully recovered from the field-induced *FM* state.

Heat capacity

Figure 11 shows the heat capacity as a function of temperature in magnetic fields of zero, 20, and 50 kOe, measured on heating after zero field cooling the sample. Consistent with dc magnetization behavior, the $C_p(T)$ data in zero magnetic field show no distinct anomalies associated with any phase transitions at low temperatures, except for the λ-type peak at ~128 K corresponding to the $AFM\rightarrow PM$ transition. A similar behavior holds for the cases with an applied magnetic field lower than 10 kOe. This result confirms that there are no obvious phase transitions below ~128 K in a magnetic field smaller than ~10 kOe. When magnetic field equals or exceeds 20 kOe, however, a sharp peak in the $C_p(T)$ data develops at low temperatures, in addition to the λ-type anomaly at ~128 K. The sharp peak shifts towards higher temperatures (~30 K in 20 kOe to ~48 K in 50 kOe), while the λ-type anomaly at ~128 K, which is observed in zero field, shifts towards lower temperatures with increasing magnetic field. The sharp peak on the $C_p(T)$ data manifests a temperature induced first-order phase transition from the *FM* state at low temperatures to the *AFM* state at higher temperatures. The behavior of heat capacity in magnetic fields between 10 and 20 kOe is quite complex and analysis of the data will be published elsewhere when it is completed.

Considering the heat capacity below ~25 K in zero magnetic field, its values are larger when compared to the data observed in 20 and 50 kOe magnetic fields, as is easily recognizable in Fig. 11. This enhancement is consistent with the cusp in dc magnetization observed at ~17.5 K in low magnetic fields (see Figs. 1 and 4). As shown in Fig. 12, the difference between the C/T values in zero field and the C/T values in an applied magnetic field H (20 and 50 kOe) exhibits broad peaks at ~17.5 K, i.e., at the same temperature

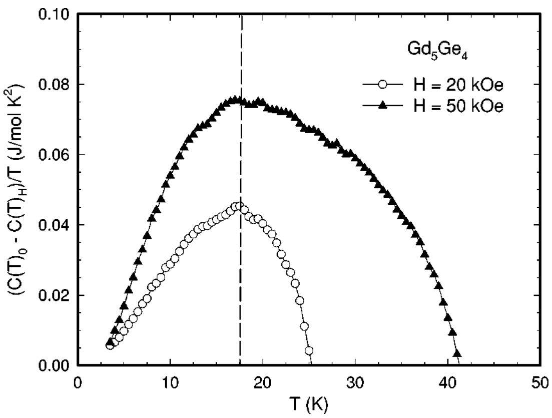

FIG. 12. The temperature dependence of the C/T difference between the zero field case and the cases with magnetic fields of 20 and 50 kOe, respectively.

as the cusp observed in the low-field dc magnetization data. Considering that Gd is an S-state ion, the likely origin of the heat capacity anomaly shown here is a spin re-orientation, e.g., from an easy plane anisotropy to an easy-axis anisotropy, or from an easy-cone anisotropy to an easy-axis anisotropy. However, this anomaly can also be due to a variation of canting angle assuming a complex magnetic structure of the material and its dependence on temperature in weak magnetic fields. The magnetization data on single crystal Gd_5Ge_4, which were obtained by Levin *et al.*,[21] are helpful since they may give a more detailed account about the origin of this anomaly.

DISCUSSION

Based on the experimental results presented above, the corresponding critical fields and/or critical temperatures can be utilized to construct the refined H-T magnetic phase diagram for Gd_5Ge_4 (see Fig. 13). Figure 13(a) is for the initial magnetization of the thermally demagnetized sample, and Fig. 13(b) is for the sample pre-magnetized at 4.5 K by a magnetic field of 56 kOe. Taking into account the nature of the *AFM* states at different temperatures, the H-T phase diagram shown in Fig. 13(a) represents a revision of that published recently by Levin *et al.*[8] It emphasizes that the initial *AFM* state at the lowest temperature, which is labeled as *AFM*-2, is different from the high temperature *AFM* state between ~ 21.3 and ~ 128 K, which is denoted as *AFM*-1. The mixture of *AFM*-1 and *AFM*-2 phases between ~ 8.6 and ~ 21.3 K is responsible for the temperature independence of the critical magnetic field in this temperature range. Both *AFM* states can be transformed into the *FM* state by the application of a magnetic field. The transition from *AFM*-2 to *FM*, induced by field, is irreversible, and the critical field decreases with increasing temperature, reaching ~ 10 kOe at ~ 8.6 K. However, the transition from *AFM*-1 to *FM* is reversible but with a hysteresis of ~ 10 kOe, and the critical field increases with increasing temperature, beginning from ~ 10 kOe at ~ 21.3 K. The sample pre-magnetized at 4.5 K, which behaves different from the thermally demagnetized sample, exhibits a mixture of *FM* and *AFM*-1 states between

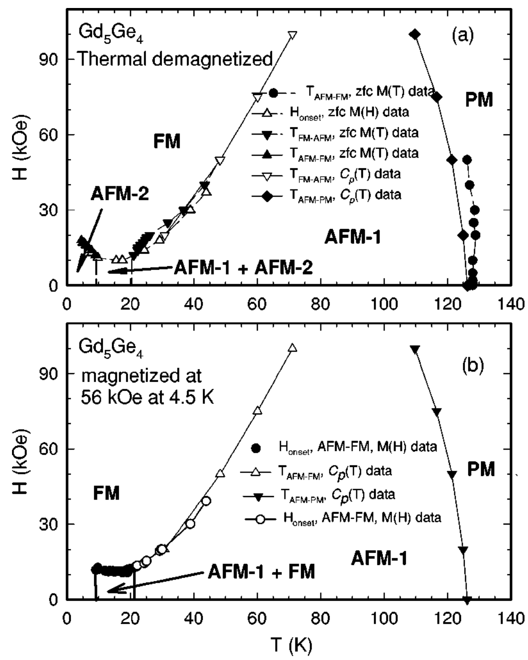

FIG. 13. The refined H-T phase diagrams for polycrystalline Gd_5Ge_4. The critical magnetic field values derived from $M(H)$ data are the onset values of the transition from *AFM* to *FM* state during the magnetic field increasing, the critical temperature data from heat capacity, or thermal magnetization data were taken on heating. (a) Thermally demagnetized sample and (b) the sample magnetized by a magnetic field of 56 kOe and after reducing the magnetic field to zero at 4.5 K.

~ 8.6 and ~ 21.3 K, and there is only one magnetic field induced *FM* state existing at temperatures below ~ 8.6 K.

In order to interpret the observed magnetic anomalies, we propose a scenario where Gd_5Ge_4 adopts a complex canted *AFM* structure at low temperature. The actual spin structure varies as a function of temperature, and assuming a possible similarity of the magnetic structure of Gd_5Ge_4 with that of Tb_5Ge_4,[13,14] spin canting disappears with increasing temperature. For example, below ~ 8 K as shown in Fig. 5, with the application of the magnetic field higher than a critical value the magnetic moments align along the direction of the magnetic field vector *via* a metamagnetic process, and then the canting is gradually eliminated as Gd-moments approach collinearly with further increasing magnetic field. At a temperature above ~ 8 K [Figs. 5(b), 6, and 7], the discontinuous magnetization disappears due to the evolution of a different magnetic structure with varying temperature.

Similar to the silicon-containing alloys in the $Gd_5(Si_xGe_{1-x})_4$ family,[3,22,23] there is a martensitic-like magnetic-structural transition in the Gd_5Ge_4 compound.[12] It may be triggered by varying temperature at a constant magnetic field, which exceeds a critical value, or by varying magnetic field at a constant temperature over a certain range of temperatures. In the frame of this knowledge, both the $FM \leftrightarrow AFM$-1 and AFM-2$\leftrightarrow FM$ transitions can be understood as the transitions between the ferromagnetic Gd_5Si_4-type orthorhombic structure and two different antiferromagnetic orthorhombic Sm_5Ge_4-type structures. These transitions are first-order type and may occur reversibly with hysteresis (at high temperatures) or irreversibly (at low temperatures). Different from other known cases in this series, the martensitic-like transition in Gd_5Ge_4 triggered by temperature can only be observed in magnetic fields above a certain value. In zero magnetic field, no temperature induced magnetic-structural transition occurs in the titled material.

Both the cusp at $\sim$17.5 K and the thermal irreversibility observed $\sim$17.5 K in the low field magnetic data may have two possible contributions. First, they may be attributed to possible pre-martensitic phenomena recalling that there is a transformation of the Sm_5Ge_4-type orthorhombic structure (low field) into the Gd_5Si_4-type orthorhombic structure (high field).[12] Second, these anomalies may be purely magnetic in nature, i.e., magnetic structure change occurs with varying temperature, as has been reported for several other Gd-containing alloys[24–26] based on the results of neutron diffraction experiments. Another mechanism is the possibility of a spin reorientation transition, e.g., from an antiferromagnet with a uniaxial anisotropy below the cusp to an antiferromagnet with an easy plane anisotropy or easy cone anisotropy above the cusp.

It is worth noting that the magnetization behavior, shown in Fig. 9 and quantified in Fig. 10, indicates the heterogeneous nature of Gd_5Ge_4 compound in the temperature range from $\sim$8.6 to $\sim$21.3 K, i.e., the partially recovered *AFM*-1 and the residual *FM* states co-exist in zero magnetic field and in fields lower than the corresponding critical values of the $AFM \rightarrow FM$ transition. The gradually increasing amount of the *AFM*-1 phase (with increasing temperature) also indirectly supports the assumption about the heterogeneity of the virgin sample, as highlighted in the H-T phase diagram in Fig. 13(a). Unlike the magnetic field induced co-existence of the *FM* and *AFM*-1 states, the co-existing *AFM*-1 and *AFM*-2 states retain the same crystal structure.[12]

The heterogeneity of magnetic structures is related to the complex crystallography of the material. As is well known, the compound Gd_5Ge_4 possesses the Sm_5Ge_4-type orthorhombic structure at room temperature[11] with lattice parameters $a = 7.6968(5)$ Å, $b = 14.831(1)$ Å, $c = 7.7851(5)$ Å. There are three nonequivalent sites for Gd ions: Gd1 in $4(c)$, Gd2 in $8(d)$, and Gd3 in $8(d)$, and three nonequivalent sites for Ge atoms: Ge1 in $4(c)$, Ge2 in $4(c)$ and Ge3 in $8(d)$, in the unit cell. Furthermore, in this naturally layered crystal structure, the layers remain unlinked (not connected) by Ge–Ge covalent-like bonds between layers. Therefore, the coupling between Gd ions within the slabs may be different from that between the slabs. As a result, Gd spins may be coupled ferromagnetically within the layers and antiferromagnetically between the layers. The assumption of the complex canted *AFM* magnetic structure of Gd_5Ge_4, however, needs further experimental verification by neutron diffraction using high energy neutron source in order to reduce the absorption cross section of the naturally occurring mixture of Gd isotopes.[24,26]

CONCLUSIONS

In the present investigation, the isothermal magnetization behavior, thermal magnetic properties, and the heat capacity have been measured on the polycrystalline Gd_5Ge_4 alloy as a function of temperature and magnetic field under various conditions. The magnetic field induced $AFM \leftrightarrow FM$ transitions, the metamagnetic behavior, and the two-component magnetization behavior have been observed in the zero-field-cooling initial $M(H)$ curves. The cusp in the zfc $M(T)$ curves in magnetic fields below $\sim$10 kOe, and thermal magnetic irreversibility between the zfc and fc dc $M(T)$ curves in various magnetic fields have been observed below $\sim$20 K. Moreover, taking into account both the reversible and irreversible nature of the related $AFM \leftrightarrow FM$ transitions, the refined H-T magnetic phase diagrams have been constructed for the material in the thermally demagnetized and in the pre-magnetized states. In order to interpret the observed magnetic anomalies in the Gd_5Ge_4 compound, an assumption has been made that at low temperatures there is a complex canted antiferromagnetic structure, and it shows complex temperature dependence. A martensitic-like structural transition, which is driven by temperature when the magnetic field exceeds a certain value ($\sim$10 kOe), or by magnetic field variation above $\sim$20 K, plays a role in the observed unusual sequence of magnetic phases.

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