Magnetic anisotropy and magnetic phase diagram of Gd5Ge4

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Magnetic anisotropy and magnetic phase diagram of Gd\(_5\)Ge\(_4\)

Abstract
The magnetization of single crystal Gd\(_5\)Ge\(_4\), which in a zero magnetic field orders antiferromagnetically at 128 K, indicates a reversible spin-flop transition when the magnetic field is along the c axis and the absence of similar transformations when the magnetic field vector is perpendicular to the c axis. This anisotropic behavior is due to variation of magnetization energy between the c axis and the a or b axes of the orthorhombic crystal caused by a different alignment of the Gd moments with respect to the magnetic field vector. The anisotropy of the antiferromagnetic state diminishes with the increasing magnetic field and temperature. The critical magnetic field for the antiferromagnetic-ferromagnetic transition is the smallest and the ferromagnetic state is most stable when the magnetic field vector is parallel to the b axis, indicating an easy magnetization direction along this axis. The anisotropy of the magnetic field-induced transformation in Gd\(_5\)Ge\(_4\) is discussed in connection with the coupled magnetic and structural transitions. Anisotropic magnetic phase diagrams along the three major crystallographic axes are constructed.

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Magnetic anisotropy and magnetic phase diagram of Gd₅Ge₄

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I. INTRODUCTION

Magnetic anisotropy is an important and intrinsic property of many rare-earth-based magnetic materials. The varying levels of anisotropy in these compounds are related to single ion anisotropies of specific lanthanide ions and/or to the anisotropy of the crystal lattice resulting from a particular crystal structure, often distinctly layered. The nonzero magnetic anisotropy of Gd-based compounds receives considerable attention because the Gd³⁺ ion has a negligible anisotropy of its 4f-electron wave functions and anisotropic magnetic properties are defined solely by the crystal lattice.

The pseudobinary Gd₅Si₄Ge₄₋ₓ compounds, as a recent example of naturally layered materials, exhibit unusually strong responses to small changes of magnetic field, such as large magnetocaloric, magnetostrictive, and magnetoresistance effects when x ≈ 2.7–11. Early experiments revealed that they are due to the magnetic field-induced first-order magnetic phase transition which in these compounds is accompanied by a simultaneous crystallographic transformation. These coupled magneto-structural transitions, depending on the value of x, magnetic field, temperature, and pressure, were found to be related to the breaking or the reforming of (Si,Ge)-(Si,Ge) covalent-like bonds between structurally well-defined, subnanometer-thick slabs that are infinite in two dimensions along the a and c axes and are stacked differently along the b axis forming three different crystal structures found in the Gd₅SiₓGe₄₋ₓ family. Despite the distinctly anisotropic crystal lattices, little is known about the related anisotropy of the physical behaviors in the Gd₅SiₓGe₄₋ₓ system.

One of the parent compounds, Gd₅Ge₄, is especially intriguing because of its peculiar magnetic properties that are clearly related to instability of the magnetic structure of the material. The magnetic ground state of Gd₅Ge₄ is believed to be antiferromagnetic (AFM). The AFM state can be transformed into the ferromagnetic (FM) state depending on the temperature and the applied magnetic field as long as the latter exceeds ~10 kOe. At the same time, the crystal structure is transformed from the Sm₂Ge₄-type to the Gd₅Si₄-type structure, with the transition showing a martensitic-like character. Below ~10 K, the magnetic-field-induced AFM-FM transition in polycrystalline Gd₅Ge₄ is irreversible, while above ~20 K the transition becomes completely reversible. Between ~10 and ~20 K, there exists a mixture of states exhibiting both irreversible and reversible AFM-FM transitions. It appears that the unusual magnetic correlations in Gd₅Ge₄ originate from the anisotropy of exchange interactions that arises from the presence of the distinctly two-dimensional slabs exhibiting varying interslab interactions and bonding.

A few basic magnetic properties of a Gd₅Ge₄ single crystal were recently investigated. It was postulated that below the Néel temperature, the magnetic moments of Gd are ferromagnetically coupled within each slab but the slabs are antiferromagnetically coupled along the c axis in low magnetic fields (H ≤ ~8 kOe). This assumption was supported by a recent microscopic study of the magnetic structure of a single crystal of Gd₅Ge₄ performed by x-ray resonant magnetic scattering measurements. Interestingly, a fully reversible spin-flop transition was observed at 4.3 K when a magnetic field of ~8.4 kOe was applied along the c direction. To date, data about anisotropy of the magnetic properties of Gd₅Ge₄ are limited to Ref. 25 which reports isothermal magnetization at 4.3 K and isofield magnetization in several fixed magnetic fields.
In this work, we study details of the magnetic anisotropy by both the isothermal $M(H)$ and isofield $M(T)$ measurements along the three principal axes of the crystal. Since the ground state of Gd$_5$Ge$_4$ is an antiferromagnet, we examine both the anisotropy of the AFM state and the anisotropy of the magneto-structural transition. Finally, the magnetic phase diagrams with the magnetic field vector applied along the three principal crystallographic axes are constructed.

II. EXPERIMENTAL DETAILS

A single crystal of Gd$_5$Ge$_4$ was grown using the tri-arc pulling technique starting with a polycrystalline ingot with the same nominal chemical composition. Polycrystalline Gd$_5$Ge$_4$ was prepared by arc melting stoichiometric amounts of high purity Gd and Ge metals under an argon atmosphere. The gadolinium metal (99.9 at.\% pure) was obtained from the Ames Laboratory Materials Preparation Center and contained the following major impurities (in parts per 10$^6$ atomic): O, 440; C, 200; H, 160; N, 90; Fe, 40; and F, 30. The Ge metal was better than 99.99 at.% pure and it was purchased from Meldform Metals, Inc. The ingot was flipped and melted several times to ensure homogeneity. The arc melted button was used as the charge material in a tri-arc furnace. A tungsten rod was used as the seed material, which resulted in a randomly oriented Gd$_5$Ge$_4$ crystal. The as-grown single crystal was oriented by back-reflection Laue x-ray diffraction and a cubelike sample with its faces parallel to the (100), (010), and (001) crystallographic planes was cut from a large single crystalline grain by the spark erosion technique. Final dimensions of the sample were 1.22 $\times$ 1.23 $\times$ 1.30 mm$^3$.

The magnetization measurements were performed in a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer, model MPMS-XL, over a temperature range of 2–300 K and a magnetic field range of 0–70 kOe. Each measurement sequence was recorded after the sample was zero field cooled (ZFC) from the paramagnetic (PM) state at 300 K. In the ZFC isothermal $M(H)$ scans, the first measurement includes the first field increase and the subsequent field reduction. The second field increase was performed immediately after the first measurement. During the measurements, the deviation of the alignment of the magnetic field vector with the crystallographic directions of the single crystal was less than $\pm 5^\circ$.

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show the isothermal magnetization curves of the ZFC Gd$_5$Ge$_4$ single crystal measured with the magnetic field vector parallel to the crystallographic $a$, $b$, and $c$ axes, respectively (magnetization data along the $b$ axis are similar to those shown in Fig. 1). The major differences are slightly lower critical magnetic fields and narrower hysteresis at 30 K and 50 K. The $M(H)$ curves exhibit the AFM-FM transition similar to that reported for polycrystals. In polycrystalline samples, however, the field-increasing branches of the ZFC $M(H)$ curves measured below $\sim 9$ K present two metamagnetic features, as illustrated in Fig. 3, for two different specimens. The first is usually observed as a nearly discontinuous transition (e.g., at $\sim 17$ kOe for 6.1 K isotherm) and the second is a continuous one, which occurs near the saturation of the magnetization (e.g., between $\sim 18$ kOe and 25 kOe for the 6.1 K isotherm). We note that a similar continuous transition in addition to a sharp metamagneticlike feature was observed in polycrystalline Gd$_5$Ge$_4$ by Hardy et al., but the origin of the anomaly was left without a discussion. Such a two-step metamagnetic transition is quite unusual and is obviously an intrinsic property of polycrystalline Gd$_5$Ge$_4$ regardless of the source of the
the two samples from Fig. 3 have been prepared from high purity Gd, while the sample in Ref. 29 was made using commercial, "99.9% pure" Gd metal. At $T \approx 9.7$ K, the second feature on the $M(H)$ curves disappears. We believe that either of the following mechanisms may be responsible for the differences in the behaviors of $M$ with $H$ in a single crystal and in a polycrystal. First, the tail-like metamagnetic features in polycrystalline samples may be related to kinetic arrest of the first-order magneto-structural transition. As temperature increases to $\sim 10$ K, thermal energy overcomes kinetic limitation and the high-field tail gradually disappears. Second, as seen in Figs. 1 and 2, the critical magnetic fields, $H_{cr}$, are different for different crystallographic directions. Furthermore, $H_{cr}$ are temperature dependent and the rates of their change with temperature are also different. Thus, the high-field $M(H)$ tails observed immediately after the sharp steps in the polycrystal data (Fig. 3) may be reflective of the magnetocrystalline anisotropy of Gd$_5$Ge$_4$ coupled with a complex preferred orientation of the grains in the as-solidified arc-melted buttons.

A. Anisotropy of the AFM state

The anisotropy of the AFM state of Gd$_5$Ge$_4$ is marked first by a spin-flop transition observed along the $c$ axis. The magnetization increases nearly linearly for the $a$ and $b$ axes with increasing magnetic field regardless of temperature, but the magnetic behavior along the $c$ axis is quite different. A nearly discontinuous step-like transition is observed at various temperature-dependent critical fields $H_{sf}$. On both sides of $H_{sf}$, the magnetization along the $c$ axis varies linearly but with a different slope. Below $H_{sf}$, the slope is much smaller, indicating a more complete compensation of the magnetic moments. This picture agrees with a model where the antiferromagnetic coupling of the Gd moments occurs along the $c$ axis, as suggested in Refs. 25 and 26. The temperature behaviors of $H_{sf}$ and dc magnetic susceptibility in the AFM state are illustrated in Figs. 4 and 5. The critical field $H_{sf}$ increases nonlinearly from $\sim 8.3$ kOe at 2 K and then saturates at 10.3 kOe between 80 K and 128 K. With increasing temperature, $dM/dH$ increases before and decreases after the spin-flop transition, leading to a gradual reduction of the step at $H_{sf}$. The $M(H)$ discontinuity becomes a minor slope.
change at $T = 120$ K and it disappears above $T_N \approx 128$ K. Extrapolating the $M$ vs $H$ behavior above $H_d$ to $H = 0$ (dotted lines in Fig. 4) shows that $M$ approaches zero as $H$ approaches zero, and therefore, the magnetic structure remains AFM with a nearly zero spontaneous magnetization but with a larger magnetic susceptibility when compared to the normal AFM Gd$_5$Ge$_4$ (i.e., the zero magnetic field state of the compound). The $M(H)$ curves for both the field-increasing and the field-decreasing branches coincide with each other, showing that the field-induced spin-flop transition is fully reversible and nonhysteretic. We note that in the second $H$-increasing measurement, the spin-flop transition along the $c$ axis is only observed above 7 K (see Fig. 2).

The anisotropy of the AFM state is also manifested in the isofield magnetization data. Figure 6 shows the ZFC heating and field cooling (FC) $M(T)$ curves measured both in low [$H=0.5$ kOe, 3 kOe, and 10 kOe, Figs. 6(a)–6(c)] and high fields [$H=20$ kOe and 50 kOe, Figs. 6(d)–6(f)]. An AFM-PM transition is observed along all three axes at $T_N$. With decreasing temperature, the $M(T)$ curves exhibit a pronounced anisotropy in low magnetic fields. No states other than the normal AFM Gd$_5$Ge$_4$ are observed in the 0.5 kOe and 3 kOe $M(T)$ curves. The same is true for the 10 kOe applied field along the $a$ axis, where a kink is observed at $\approx 14$ K, below which the ZFC and FC $M(T)$ curves diverge slightly [Fig. 6(a)]. The $c$-axis $M(T)$ curve [Fig. 6(c)] exhibits a reversible spin-flop transition at $\approx 50$ K and a kink at $\approx 14$ K, which is similar to that observed along the $a$ axis in Fig. 6(a). When a 10 kOe magnetic field is applied along the $b$ axis [Fig. 6(b)], Gd$_5$Ge$_4$ is no longer in a purely AFM state. The magnetic field dependence of the spin-flop transition is further illustrated in more detail in Fig. 7, in which the 0.5, 3, and 10 kOe data from Fig. 6 are also included.

With the occurrence of the spin-flop transition, Gd$_5$Ge$_4$ exhibits at least two distinct AFM states (see Figs. 4 and 7).

When $H < 8.3$ kOe, the “normal” AFM state is stable at all temperatures below $T_N$. When $H > 10.3$ kOe is applied along the $c$ axis, the spin-flop AFM structure exists in the same temperature range and when $8.3$ kOe $< H < 10.3$ kOe, the stability of either state becomes temperature dependent. As deduced from the results presented in Figs. 4 and 7, the magnetic moments of Gd below 128 K are coupled antiferromagnetically along the $c$ axis when the applied field is below 8.3 kOe. With the spin-flop transition, the AFM coupling of the Gd magnetic moments changes its direction from parallel to perpendicular to the $c$ axis.

To explore the details of the anisotropy of the AFM state, the 0.5 kOe ZFC and FC $M(T)$ curves are shown together in Fig. 8(a). We note that the FC $M(T)$ curves diverge from the ZFC curves below $\approx 60$ K for the $a$ and $c$ axes, and below $\approx 40$ K for the $b$ axis. On the other hand, the $H=3$ kOe and higher field $M(T)$ curves follow one another closely as long as Gd$_5$Ge$_4$ remains AFM for both ZFC and FC states down to $\approx 14$ K, below which they become slightly divergent (also see Fig. 6). Furthermore, when the magnetic field is parallel to the $a$ or the $b$ axis, the magnetization in the AFM state decreases with increasing temperature. Chattopadhyay et al. report a similar behavior for a polycrystalline sample, attributing this to spin fluctuations and FM correlations apparently present in the sample. The 0.5 kOe $M(T)$ curves for the $a$ and $b$ axes diverge below $T_N$ [see Fig. 8(a)], which is different from the 8 kOe data of Ref. 25 and our data above 3 kOe [Fig. 8(b)] indicating that the $M(T)$ curves in the AFM state above 3 kOe always nearly overlap for the $a$ and $b$ axes. That is, the anisotropy of the AFM state between the $a$ and the $b$ axes at low temperatures and low fields is weak, and a 3 kOe field is high enough to completely
suppress this anisotropy. When the field vector is applied along the c axis, the magnetization increases with increasing temperature, resembling the earlier reported results.\textsuperscript{25} Extrapolating the 0.5 kOe $|H|c$ $M(T)$ curve to zero temperature, suggests that the magnetization remains larger than zero due to the incompletely compensated moments. A similar conclusion can be drawn from the 0.1 kOe data reported in Ref. 26. The difference of the magnetization between the $a$ and the other two axes, as shown in the inset of Fig. 8(a), varies almost linearly below $T_N$, indicating that the anisotropy in the AFM state increases nearly linearly with decreasing temperature.

The magnetic anisotropy in the AFM state observed in the isothermal $M(H)$ and isofield $M(T)$ measurements can be understood by considering the configuration of Gd moments with respect to the external magnetic field. When the magnetic field is parallel to the $a$ or $b$ axis, the spin axis of the Gd moments (i.e., the c axis) is perpendicular to the field vector. Thus, the magnetization decreases with increasing temperature as follows from Néel’s model\textsuperscript{32} and from possible FM spin fluctuations in the sample. However, when the field vector is applied along the $c$ axis, the spin axis of the Gd moments is also parallel to the field vector. This AFM state is denoted as the normal AFM state because of its similarity to the classical magnetic behavior of an antiferromagnet [see Fig. 8(a)]. Since the magnetic susceptibility along the $a$ axis, $\chi_a$ (or the $b$ axis, $\chi_b$), is always larger than that along the $c$ axis, $\chi_c$, the energy of magnetization below $T_N$ given by $E = -(1/2)\chi H^2$ is always lower for the $a$ axis or $b$ axis than for the $c$ axis. The thermodynamically stable system must have the lowest magnetic energy, and therefore, the whole spin arrangement along the $c$ axis tends to rotate so as to make its spin axis perpendicular to the external field. Néel\textsuperscript{32} predicted that such a flopping of the spin axis should occur when the field reaches some critical value. The critical field is determined by the magnitude of the magnetocrystalline anisotropy. For the present sample, the required critical field lies between $\sim 8.3$ kOe and $\sim 10.3$ kOe for $2K < T < T_N$. Accordingly, the directions of the Gd moments in the spin-flop AFM state (within the $ab$ plane) are perpendicular to the magnetic field vector (i.e., the $c$ axis). The magnetic behavior of the spin-flop AFM state is therefore expected to be similar to that along the $a$ and $b$ axes [see Figs. 5(b) and 8(b)], where the magnetic field vector is also perpendicular to the directions of the Gd moments. Therefore, the AFM state anisotropy is considerable only at low temperatures and in low magnetic fields. Raising the temperature and the magnetic field decreases the differences in the magnetic energy between the $a$ axis (and the $b$ axis) and the $c$ axis, and therefore, reduces the magnetocrystalline anisotropy of the compound in the AFM state.
B. Anisotropy of the AFM-FM transition in Gd$_5$Ge$_4$

The anisotropy of the magnetic field-induced AFM-FM transition is prominent. As shown in Figs. 1 and 2, the field induced AFM-FM transition is not as sharp as one might expect for a single crystal, i.e., it starts at a certain critical field $H_{c1}$ and ends at a higher critical field $H_{c2}$. The critical fields decrease with increasing temperature, reaching directionally dependent minima at $\sim$14 K, and above this temperature, both $H_{c1}$ and $H_{c2}$ begin to increase with temperature (see Fig. 9). The values of the critical fields vary with the crystallographic directions. Between 2 K and 50 K, the values of $H_{c1}$ and $H_{c2}$ for the $b$ axis are notably lower than those for the $c$ axis, and the latter are lower than those along the $a$ axis. The minimum of $H_{c1}$ and $H_{c2}$ along the $b$ axis indicates that the compound is more easily converted into the FM state with field applied in this direction compared with the other two axes. The difference between the critical fields along different axes is large at low temperature, gradually diminishing as temperature rises, indicating the reduction of the magnetocrystalline anisotropy.

During the second increase of the magnetic field, the magnetization follows the first demagnetization curve at 2 K (not shown in Figs. 1 and 2 for conciseness), signaling that the entire sample remains in the FM state, i.e., the field-induced AFM-FM transition is irreversible and once the FM phase is formed, it is stable at this temperature after removing the magnetic field. However, the magnetization curves at 4 K do not precisely follow the first demagnetization path. Above 4 K, a steplike ferromagnetic behavior is seen in low fields. The saturation magnetization of the low-field FM state, estimated as shown by the dashed lines in Figs. 1 and 2, decreases with temperature and nearly disappears at $\sim$14 K,

![Figure 7](image7.png)

**FIG. 7.** (Color online) The ZFC heating $M(T)$ curves of Gd$_5$Ge$_4$ single crystal measured when the magnetic field vector is parallel to the $c$ axis.

![Figure 8](image8.png)

**FIG. 8.** (Color online) (a) The ZFC heating and FC $M(T)$ curves of the single crystal of Gd$_5$Ge$_4$ measured at $H=0.5$ kOe. The inset is the ZFC magnetization difference between $M_c$ and $M_a(M_b)$. (b) The $M(T)$ curves in the AFM state extracted from the $M(T)$ curves shown in Fig. 6.

![Figure 9](image9.png)

**FIG. 9.** (Color online) The anisotropy and temperature dependencies of the critical magnetic fields ($H_{c1}$, left and $H_{c2}$, right) of the AFM-FM transition in the ZFC single crystal of Gd$_5$Ge$_4$. 

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pointing to the temperature associated with the minimum of $H_3$ and $H_2$. Hence, between $\sim 4 \text{ K}$ and $\sim 14 \text{ K}$, the first application of field induces the FM phase in the entire AFM sample. When the field is removed, a fraction of the sample volume is converted back into the AFM state, whereas the rest of the sample still remains in the FM state. That is, both the irreversible and reversible AFM-FM transformations coexist in this temperature range. Considering that $dM/dH$ curves in the steplike magnetization region show no spin-flop anomaly below 7 K and that the AFM state involved in the AFM-FM transition along the $c$ axis is the spin-flop AFM state, it is likely that the recovered AFM state is only the spin-flop AFM state below 7 K and a mixture of the normal state, it is likely that the recovered AFM state is only the spin-flop AFM state below 7 K and a mixture of the normal and the spin-flop AFM states above 7 K. Above $\sim 14 \text{ K}$, the $M(H)$ curves in the second application of field nearly coincide with those in the first field-increasing measurement because there is no residual FM phase after the first measurement cycle. Thus, the AFM-FM transition becomes fully reversible above $\sim 14 \text{ K}$ exhibiting directionally dependent hysteresis. We recall that a polycrystalline sample also shows a similar mix of reversibility and irreversibility of the AFM-FM transition, but the temperature range where the two types of transitions coexist is between $\sim 10 \text{ K}$ and $\sim 20 \text{ K}$.\(^{18,23}\)

The residual contents of the FM phase along the three axes, evaluated from the low field magnetization steps in the second $H$-increasing $M(H)$ curves by computing a ratio of the saturation magnetization at individual temperatures, are illustrated in Fig. 10. The temperature dependencies of the residual FM phase content exhibit inverse $S$ shapes, which is different when compared with a polycrystalline sample, where the residual FM content, derived by initially magnetizing the sample at 4.5 K by a 56 kOe field and then warming in a zero field up to the measurement temperature, varies linearly between $\sim 10 \text{ K}$ and $\sim 21 \text{ K}$.\(^{23}\) Notably, the residual FM amount also shows a directional dependence: between 4 K and 14 K, and especially from 7 to 10 K, it is the largest along the $b$ axis and the smallest along the $c$ axis. As a result, the reversibility of the AFM-FM phase transition is best when the field is applied along the $c$ axis and it is most incomplete when the magnetic field is applied parallel to the $b$ axis. Different factors may play a role in the varying completion of the FM $\rightarrow$ AFM transition upon removal of the magnetic field between 4 and 14 K. First, the maximum retention of the FM phase with the magnetic field applied along the $b$ axis is consistent with this being the easy magnetization direction (see next paragraph). Second, the best reversibility with the magnetic field applied along the $c$ axis is commensurate with the recovery of the normal AFM state occurring around 8.5 kOe in this temperature range [see Fig. 5(a)]. Finally, even though the domain structure of the ferromagnetic Gd$_5$Ge$_3$ is unknown, it is safe to assume that it is highly anisotropic and similar to that observed in a single crystal Gd$_2$Si$_2$Ge$_2$. The latter has the same crystal structure in the ferromagnetic state and exhibits stripe domains when viewed along the $a$ axis, a rosette domain pattern typical of a soft uniaxial ferromagnet when viewed along the $b$ axis, and practically no magnetic contrast when viewed along the $c$ axis.\(^{33}\)

We now discuss the anisotropy of the FM-AFM transition based on the results described above. In Fig. 11 the $H$-decreasing $M(H)$ branches are compared at several temperatures. The magnetization always exhibits a rapid fall off at a certain critical field $H_3$. Below $\sim 4 \text{ K}$, the AFM-FM transition is irreversible and the FM $\rightarrow$ AFM transition does not occur at all. The critical fields are anisotropic, i.e., $H_3$ ($b$ axis)<$H_3$ ($a$ axis)=$H_3$ ($c$ axis). Since Gd$_5$Ge$_4$ is a collinear ferromagnet above $H_3$, the same fields are expected to be the values where magnetization reaches saturation during the second field application at these temperatures. Therefore, the system exhibits a strong ferromagnetic anisotropy between the $b$ axis and $a$ or $c$ axis, showing that the $b$ axis is the easy magnetization direction in the FM state of Gd$_5$Ge$_4$. The $M(H)$ curves nearly overlap with each other for the $a$ axis and the $c$ axis, showing no anisotropy between these two “hard magnetization” directions. Between $\sim 4 \text{ K}$ and 14 K, where a certain fraction of the sample preserves the FM state, the system shows behavior similar to that below 4 K. At and above 14 K, Gd$_5$Ge$_4$ maintains the notable anisotropy of the FM $\rightarrow$ AFM transition that now starts at $H_3$ and ends at $H_4$. The $a$-axis $M(H)$ demagnetization curve no longer overlaps with the $c$-axis $M(H)$ curve. The values of $H_3$ and $H_4$ remain the smallest along the $b$ axis at temperatures as high as 30 K [Fig. 11(d)].

The anisotropy of the AFM-FM transition is also manifested in the $M(T)$ curves shown in Fig. 6. The 50 kOe $M(T)$ curves exhibit sharp FM-AFM transitions at $T_C=\sim 50 \text{ K}$. The ZFC data and the FC data almost overlap showing little to no hysteresis, which is different from polycrystalline data, where a hysteresis of about $\sim 8 \text{ K}$ was observed.\(^{18}\) With magnetic field decreasing to 20 kOe, directionally dependent temperature hysteresis gradually sets in. The hysteresis is larger along the $a$ axis than the other two axes, yet it always remains lower than that of a polycrystal. The ZFC $M(T)$ curves for the $a$ and $c$ axes exhibit an AFM $\rightarrow$ FM transition followed by an FM $\rightarrow$ AFM transition, while the FC $M(T)$ curves only exhibit an AFM $\rightarrow$ FM transition and the sample

![Image](https://i.imgur.com/5Q5Q5Q5.png)
remains in the FM state down to the lowest temperature, i.e., \( \sim 4 \text{ K} \). This is consistent with the isothermal magnetization results, where Figs. 1(a) and 2(a) show that the 20 kOe field is below \( H_{c1} \) of the low temperature \( M(H) \) curves, thus the FM state cannot be induced by isothermally magnetizing the sample up to 20 kOe at 4 K along the \( a \) and \( c \) axes. As temperature increases beginning from 4 K, \( H_{c1} \) for these two directions lowers, soon becoming smaller than the 20 kOe field surrounding the sample, thus resulting in the temperature-induced AFM-FM transformation. The high temperature FM-AFM transition occurs when the critical magnetic fields begin to increase again above 14 K eventually exceeding 20 kOe. When \( H=10 \text{ kOe} \), the \( b \)-axis \( M(T) \) curves still show AFM-FM and FM-AFM transitions, while the \( a \)- and \( c \)-axes \( M(T) \) curves no longer show any FM state.

It is believed that the observed anisotropy is related to the anisotropy of the two crystal structures adopted by the \( \text{Gd}_5\text{Ge}_4 \) system in the AFM and FM states, both of which are layered with the layers extending in the \( ac \) plane that are stacked differently along the \( b \) axis. The arrangement of Gd atoms along the \( a \) and \( c \) axes is quite similar. Hence, it is feasible that in the spin-flop AFM state, the Gd moments remain ferromagnetically coupled within the layers but the interlayer coupling becomes AFM along the \( a \) axis. Hence, during the AFM-FM transition, the system changes its magnetic state from AFM coupling along the \( a \) axis to become a collinear ferromagnet along the \( c \) axis when the magnetic field is applied along this direction, whereas when the magnetic field is parallel to the \( a \) axis, the magnetic state is changed from the AFM state along the \( c \) axis to the collinear FM state along the \( a \) axis. In both cases, the Gd moments rotate within the \( ac \) plane without the involvement of the \( b \) axis. This feature results in the similarity of the anisotropy of the FM state below 4 K, as seen in Fig. 11(a). The larger \( H_{c1} \) and \( H_{c2} \) along the \( a \) axis compared to the \( c \) axis (Fig. 9) is likely related to the anisotropy of the lattice constants and their variation during the AFM-FM transition, in which the value of \( a \) decreases from 7.68 Å in the AFM state to 7.54 Å in the FM state, while the value of \( c \) increases from 7.76 Å in the AFM state to 7.81 Å in the FM state at 6.1 K.21 The lattice expansion-related energy barrier between AFM and

![Diagram](image1)

**FIG. 11.** (Color online) The \( H \)-decreasing \( M(H) \) curves of the single crystal of \( \text{Gd}_5\text{Ge}_4 \) measured at \( T=4 \text{ K}, 8 \text{ K}, 14 \text{ K}, \) and 30 K (see also Figs. 1 and 2).

![Diagram](image2)

**FIG. 12.** (Color online) The temperature dependencies of the reciprocal magnetic susceptibility \( H/M \) of the \( \text{Gd}_5\text{Ge}_4 \) single crystal measured at \( H=0.5 \text{ kOe} \). The solid lines represent the Curie-Weiss fit.
The arrangement of the Gd atoms along the $b$ axis is quite different from the other two directions. When the magnetic field vector is applied along this axis, the system changes its magnetic state from AFM state along the $c$ axis to the collinear FM state along the $b$ axis, which is also quite different from the case when the field vector is parallel to the other two axes. The Ge–Ge bonds between the layers stacked along the $b$ axis are broken before the AFM-FM transition. Once the FM phase is established, the $H$ values of $H_{c1}$ and $H_{c2}$ first decrease and then increase with the increasing temperature. Both exhibit a minimum around 14 K for the three axes. An extrapolation of the curves along each axis, shown by the dashed lines in Figs. 13(a)–13(c), results in a critical point with $H_{c1} \approx 140$ kOe, above which the AFM state is completely suppressed, and $T_{c1} \approx 90$ K. It is worth noting that a recent high field study of a low purity single crystal of Gd$_5$Ge$_4$ along the three principal crystallographic axes, in which the symbols ($\ast$) and ($\times$) are the critical fields $H_{c1}$ and $H_{c2}$, respectively, obtained from $M(H)$ curves, the symbols ($\blacksquare$) are the data derived from the $M(T)$ curves, and the symbols ($\blacktriangle$) are the data of $H_d$. The plots on the left are for the initial magnetization of the ZFC single crystal. Extrapolations for magnetic fields exceeding 5 T shown by the dashed lines assume that both the AFM-FM and AFM-PM boundaries follow the corresponding boundaries established for polycrystalline Gd$_5$Ge$_4$ (Refs. 17 and 23). The plots on the right are for the second isothermal magnetization of the same crystal with only the low-temperature parts shown for clarity because above ~14 K the initial magnetization and the second magnetization diagrams are indistinguishable for the same direction.

FIG. 13. (Color online) The $H$-$T$ magnetic phase diagrams of single crystal of Gd$_5$Ge$_4$ along the three principal crystallographic axes, in which the symbols ($\times$) and ($\circ$) are the critical fields $H_{c1}$ and $H_{c2}$, respectively, obtained from $M(H)$ curves, the symbols ($\blacksquare$) are the data derived from the $M(T)$ curves, and the symbols ($\blacktriangle$) are the data of $H_d$. The plots on the left are for the initial magnetization of the ZFC single crystal. Extrapolations for magnetic fields exceeding 5 T shown by the dashed lines assume that both the AFM-FM and AFM-PM boundaries follow the corresponding boundaries established for polycrystalline Gd$_5$Ge$_4$ (Refs. 17 and 23). The plots on the right are for the second isothermal magnetization of the same crystal with only the low-temperature parts shown for clarity because above ~14 K the initial magnetization and the second magnetization diagrams are indistinguishable for the same direction.
polycrystalline Gd₅Ge₄ sample by Casanova et al.⁴⁶ reported the same coordinates of the tricritical point: $H_{tc}$ = ~140 kOe and $T_{tc}$ = ~90 K.

In the $H$-$T$ diagrams representing the second magnetization, the AFM-PM transition boundary is the same as that of the initial magnetization and is hence omitted for clarity in Figs. 13(d)–13(f). The low-temperature parts in each of these three diagrams where the AFM state is partially recovered after the first application of the magnetic field can be regarded as a superposition of a series of discrete diagrams, which is illustrated in Fig. 14. In each of these diagrams, there is no coexistence of the AFM and FM states but the AFM phase region simply extends to a different lowest temperature, $T_i (i = 1, 2, \ldots, m)$, where the AFM phase transforms into the FM phase isothermally. The result of the superposition is that between ~4 K and ~14 K, there exists a mixture of FM and AFM states, as is observed experimentally. Considering that the amounts of the recovered FM phase vary as shown in Fig. 10, a fraction of the sample volume characterized by the diagrams where $T_i$ is ~6 K to ~8 K is greater compared with diagrams having $T_i$ between 4 K and 6 K and between 8 K and 14 K. This deviation from a monotonic distribution of $T_i$’s is likely associated with a peculiar microstructure and/or stress fields distributed anisotropically across the single crystal. We note that in the polycrystalline samples, the linear variation of the residual FM phase with temperature between ~10 K and ~21 K (Refs. 18 and 23) suggests that the sample fraction matching each discrete diagram is the same, as is expected for a polycrystal with a large number of randomly oriented and sized crystallites. In addition, according to Chattopadhyay et al.,³⁰ the kinetics of the AFM-FM transition is arrested at low temperatures, thus the residual FM state shown in Fig. 10 may actually the trapped FM state. Obviously, the effect of kinetic arrest, if any, of the AFM-FM transition is weaker in the single crystal (starts at ~14 K) than in the polycrystal (starts at ~21 K). Note that temperatures at which the kinetic arrest develops are different although the range of temperatures over which the system becomes completely arrested is nearly identical ($\sim$10 K for the single crystal and $\sim$11 K for the polycrystal). In the single crystal, the FM phase is arrested very rapidly when temperature is reduced to ~8 K, while the trapping process in the polycrystal is much more gradual, which correlates with the simpler Sm₂Ge₂-type (AFM)/Gd₂Si₂-type (FM) domain structure in the single crystal compared to the polycrystal.

The anisotropy of the phase diagram is noticeable (see also Fig. 9). The values of $H_{c1}$ and $H_{c2}$ along the three axes are different at the same temperature. The AFM state with field along the $c$ axis is divided into two regions—normal AFM and spin-flop AFM states. From the $H$-$T$ diagram of the initial magnetization [Fig. 13(c)], when $T < T_N$, the spin-flop transition from the normal AFM state to the spin-flop AFM state can be observed in the $M(H)$ curves along the $c$ axis. The spin-flop transition can be also observed in the $M(T)$ curves when $8.3 \text{kOe} < H < 10.3 \text{kOe}$. From the $H$-$T$ diagram of the second magnetization [Fig. 13(f)], the spin-flop transition can be only observed in the temperature range $7 K < T < T_N$ in the $M(H)$ curves. When $4 K < T < 7 K$, the residual AFM state is only retained in the spin-flop AFM state. Therefore, the increase of the reversibility of the AFM-FM transition with temperature increases the content of normal AFM phase.

IV. CONCLUSIONS

A reversible spin-flop transition along the $c$ axis occurs in a single crystal of Gd₅Ge₄ at various magnetic fields ($8.3 \text{kOe}$–$10.3 \text{kOe}$) and temperatures (2 K–128 K), which is not observed when the field is applied along the $a$ and $b$ axis. This anisotropy can be understood by considering the configuration of the Gd moments in the AFM state with respect to the magnetic field vector. In the normal AFM state, the configuration of the Gd moments along the $c$ axis is different from the AFM state along the $a$ and $b$ axes. Increasing temperature reduces the magnetization difference between these axes, and thus, reduces the anisotropy of the AFM state. In the spin-flop AFM state, the configuration of
the Gd moments along the $c$ axis becomes similar to that along the $a$ and $b$ axes in the normal AFM state, resulting in the similarity of the magnetic properties in the AFM state. Thus, increasing the magnetic field effectively decreases the anisotropy of the AFM state. The fully irreversible AFM-FM transition is observed at low temperatures (below $\sim 4$ K); above $\sim 14$ K, the same transformation becomes fully reversible. Between $\sim 4$ and $\sim 14$ K there is a mixture of both transitions. The resultant residual FM content is larger for the $b$ axis than for the $a$ and $c$ axes at the same temperature, and accordingly, the critical field for the AFM-FM transition along the $b$ axis is smaller than that along the other two axes. In the FM state, the $b$ axis is the easy magnetization direction of the compound. The anisotropy of the AFM-FM transition is consistent with the anisotropic features of the distinctly layered crystal structures of the two polymorphic modifications of the compound despite negligible single ion anisotropy of the Gd$^{3+}$ ion. The magnetic phase diagrams exhibit clear anisotropy.

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