Angular dependence of the spin-flop transition and a possible structure of the spin-flop phase of Gd₅Ge₄

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Abstract
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Comments
Angular dependence of the spin-flop transition and a possible structure of the spin-flop phase of Gd$_5$Ge$_4$

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INTRODUCTION

As early as 1936, Néel\textsuperscript{1} predicted that in a uniaxial anisotropic antiferromagnet where magnetic moments are coupled with the crystal lattice, a first order spin-flop transition should occur at a certain critical magnetic field, $H_{sf}$, when the magnetic field is applied along the antiferromagnetic (AFM) coupling direction, i.e., along the AFM easy axis. As a result of the spin-flop transition, the directions of spin moments of the two sublattices abruptly change from their antiparallel configuration in which the moments are collinear with the external field to a new spin-flop configuration in which the moments remain antiparallel but become perpendicular or nearly perpendicular to the magnetic field vector. The spin-flop transition was later experimentally observed in CuCl$_2 \cdot 2$H$_2$O.\textsuperscript{2–5} The phenomenon perhaps is best manifested in several transition metal systems such as MnF$_2$ (Refs. 6–8) and FeF$_2$,\textsuperscript{9} and current research activities on spin-flop transformations are extended toward many low dimensional systems.\textsuperscript{10–12} As in the past, spin-flop transformations remain an interesting subject for both theoretical and experimental research.

Gd$_5$Ge$_4$ is one of the two parent compounds of the fundamentally important and potentially useful pseudobinary magnetocaloric alloys Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$.\textsuperscript{13–15} This binary gadolinium germanide has been broadly studied because of its intriguing physical properties that are intimately related to a peculiar low dimensional crystallography. The distinctly layered crystal structure that the system adopts in the paramagnetic state can be described as a stacking of weakly interacting identical slabs that are infinite in the $ac$ plane but are less than 1 nm thick along the $b$ axis.\textsuperscript{16–18} In the original study by Holtzberg et al.,\textsuperscript{19} the authors suggested that the ground state of Gd$_5$Ge$_4$ is AFM, although the positive Weiss temperature determined from the Curie-Weiss behavior points to a ferromagnetic ground state. Recently, this apparently contradictory result has been explained by the fact that the Gd moments are coupled ferromagnetically within the slabs, while the Gd moments between the slabs are coupled antiferromagnetically along the $c$ axis.\textsuperscript{20–25} This AFM configuration was identified both by macroscopic dc magnetization measurements\textsuperscript{26,27} and microscopic x-ray resonant magnetic scattering experiments\textsuperscript{28} thus showing that zero-field-cooled Gd$_5$Ge$_4$ is a uniaxial antiferromagnet. In the AFM state, the compound preserves the same crystal structure as in the paramagnetic state.\textsuperscript{29,30} However, when Gd$_5$Ge$_4$ is magnetized at low temperatures by a magnetic field exceeding 12 kOe,\textsuperscript{20–24,26,27,29,30} or is exposed to a hydrostatic pressure in excess of 10 kbar,\textsuperscript{31} it becomes ferromagnetic (FM). The FM ordering is accompanied by a simultaneous martensitic-like change of its crystal structure. The latter occurs by shearing of the neighboring slabs along $a$ in opposite directions,\textsuperscript{29,30} hence creating a new layered crystal structure where the slabs themselves remain unchanged but the inter-slab exchange interactions become much stronger.\textsuperscript{25} These magnetic field and pressure induced transformations are unusually sharp, which is related to the existence of a nonergodic kinetically retarded magnetic glassy state at low temperature.\textsuperscript{32}

Unlike the interplay between the paramagnetic (PM), AFM, and FM states of Gd$_5$Ge$_4$, which is relatively well studied,\textsuperscript{20–32} the nature of the spin-flop transition, which was first reported by Levin et al.,\textsuperscript{26} is much less understood. This transition occurs in the AFM state only when the magnetic field is applied along the $c$ axis. Interestingly, the spin-flop transformation remains completely unaffected by the kinetic retardation that affects the AFM-FM transition.\textsuperscript{27,33} The magnetic phase diagram with the magnetic field vector parallel to the $c$ axis (Fig. 1) shows that the FM phase orders into the normal AFM phase below $T_N=128$ K in low magnetic fields, but it is converted into a spin-flop AFM phase in fields higher than $\sim$8 kOe. Levin et al.\textsuperscript{26} suggested that in the
spin-flop state, the AFM coupling axis coincides with the $a$ axis, which was logical considering that the moments then have to rotate in the planes of the slabs rather than out of the planes of the slabs. The AFM coupling axis is perpendicular to the field vector in the spin-flop phase, but the magnetization of each sublattice is slightly tilted away from the spin coupling axis ($a$) due to the application of the magnetic field. To date, this model has not been verified experimentally.

In a uniaxial antiferromagnet, where the anisotropy energy is usually small compared to the generally isotropic exchange energy, the first order spin-flop transition can be observed only over a small range of tilt angles when the field vector remains perpendicular to the hard axis but is tilted away from the AFM easy axis toward the next easiest axis (i.e., toward the spin-flop axis). Here, we investigate angular dependence of the spin-flop transition in Gd$_5$Ge$_4$. In addition, owing to the distinctly layered crystal structure of Gd$_5$Ge$_4$, a different behavior is expected when the magnetic field is tilted away from the $c$ axis (AFM easy axis) toward the $b$ axis when compared to the magnetic field tilted away from the $c$ axis toward the $a$ axis. These experiments should verify an earlier prediction (by Levin et al.) that the microscopic magnetic structure of the spin-flop AFM phase is the result of rotating the AFM coupled moments in the $ac$ plane, as shown schematically in Fig. 1, rather than in the $ab$ plane.

**EXPERIMENTAL DETAILS**

A cubelike single crystal of Gd$_5$Ge$_4$ ($0.9 \times 1.0 \times 1.0$ mm$^3$) with its faces normal to the principal crystallographic axes and directions of magnetic field vectors was extracted from a crystal grown using the tri-arc pulling technique. Details about the basic characterization, orientation, and preparation of the specimen are given elsewhere. The magnetization measurements were performed using a superconducting quantum interference device magnetometer, MPMS-XL manufactured by Quantum Design, Inc. Before each measurement, the sample was zero-field cooled from the paramagnetic state at 300 K to the desired temperature. The misalignment between the crystallographic axes and directions of magnetic field vectors was estimated to be less than 5°.

**EXPERIMENTAL RESULTS**

Figures 2 and 3 show the field dependencies of the magnetization of a Gd$_5$Ge$_4$ single crystal measured at 2 K when the field vector was gradually tilted away from the $c$ axis toward the $b$ axis (the $cb$ plane isotherms) and away from the $c$ axis toward the $a$ axis (the $ca$ plane isotherms), respectively. All of the $cb$ plane $M(H)$ curves (Fig. 2) exhibit non-linearity in low fields (less than $\sim 4$ kOe), revealing the presence of a small amount of the FM Gd$_5$Ge$_4$ phase that precipitates in the AFM matrix during zero-field cooling. Around 20 kOe, the $M(H)$ curves show signs of an upturn, indicating the onset of the well-known and well-characterized field induced AFM→FM phase transformation. For $\theta=0$, i.e., when the magnetic field vector is applied along the $c$ axis, a nearly discontinuous steplike transition is observed at $H_d=8.3$ kOe, which is a signature of a first order spin-flop transition and whose temperature behavior was established in an earlier report (also see Fig. 1). With an increase of the tilt angle $\theta$ between $H$ and $c$, the magne-
tization in the AFM state is increased, but in the spin-flop state, the magnetization remains nearly equal to that of \(H=0\). This leads to a gradual reduction of the magnetization discontinuity at \(H_{sf}\). However, judging from the sharpness of the jump of the magnetization, the spin-flop transition maintains its first order character. Regardless of the angle \(\theta\), the \(H\)-decreasing \(M(H)\) curves nearly follow the \(H\)-increasing ones, showing the nearly complete reversibility of the spin-flop transition (see, for example, the two curves shown for \(\theta=40^\circ\)). We also note that the first order reversible spin-flop transition is observed at higher temperatures, as illustrated in the inset of Fig. 2 for \(T=30\) K.

At 2 K, \(H_{sf}\) increases nonlinearly with \(\theta\) as long as the field vector is confined in the \(cb\) plane, as shown in Fig. 4(a). Extrapolation of the \(H_{sf}\) vs \(\theta\) curve to 25 kOe, which is the critical field for the AFM→FM transition with the field vector parallel to the \(b\) axis, leads to \(\theta \approx 65^\circ\). This suggests that the spin-flop transition should disappear when \(\theta > 65^\circ\), which is consistent with the results shown in Fig. 2. The components of the vector \(H_{sf}\) are plotted in Fig. 4(b), indicating a weak and nearly linear (from 8.3 kOe at \(\theta=0\) to 9.8 kOe at \(\theta=60^\circ\)) dependence of its projection along the \(c\) axis.

When the magnetic field vector is tilted away from the \(c\) axis toward the \(a\) axis, i.e., when it is confined in the \(ca\) plane and therefore is coplanar with the slabs, a sharp spin-flop transition is only observed within a narrow range of the tilt angles, i.e., \(0 < \theta < 20^\circ\) (Fig. 3). Upon further increasing the tilt angle, the magnetization begins to exhibit a gradual and smooth transition from the normal AFM state to the spin-flop AFM state, i.e., the spin-flop transition becomes continuous and occurs over a relatively wide range of fields. Nearly the same behavior is observed at 30 K (see the inset of Fig. 3). All of these are consistent with a changeover from a first order transformation at low \(\theta\) to a second order transformation at large values of \(\theta\), which is quite different from the behavior observed when the field was applied in the \(cb\) plane. When \(\theta\) exceeds 60°, the spin-flop transition is no longer recognizable, and all magnetization curves merge into that of \(\theta=90°\) (i.e., when \(H||a\) (see Fig. 3). Obviously, the second order spin-flop transition is also reversible, as shown in Fig. 3 for \(\theta \approx 20°\).

For a continuous spin-flop transition, we define the field where the \(dM/dH\) exhibits a maximum as \(H_{sf}\). A plot of \(H_{sf}\) vs \(\theta\) is shown in Fig. 4(a). With increasing \(\theta\), the value of \(H_{sf}\) initially increases slowly and then nearly saturates around 10 kOe [Fig. 4(a)], never approaching the critical field \(H_{c}\) \(\approx 31\) kOe (Ref. 27) for the AFM→FM transition with the magnetic field vector parallel to \(a\). The projection of the vector \(H_{sf}\) along the \(c\) axis increases first for \(0 < \theta < 20^\circ\) and
The field increases. In Fig. 5 measurements in the cb plane. Within the slabs, the magnetic field depends on the orientational relationships between a normal AFM phase and a spin-flop AFM phase in a quasi two-dimensional square lattice, i.e., as long as the magnetic field remains below the critical spin-flop field for $\theta \approx 0$. When the magnetic field increases to 8.5 kOe and higher, a plateau in magnetization develops starting from $\theta \approx 0$ and the length of the plateau increases as the field increases. The plateau is followed by a spin-flop transition, which is characterized by a sharp drop of the magnetization, from the magnetoelastic coupling that arises from the competition between the anisotropy of the layered crystal structure and single ion anisotropy. Thus, the prediction by Levin et al., which was made without direct evidence, was correct, and the results presented above do confirm that the $a$ axis is indeed the spin-flop axis of Gd$_4$Ge$_3$.

Based on the experimental results presented above, we conclude that the nature of the spin-flop transition in Gd$_4$Ge$_3$ is strongly dependent on the orientational relationships between the direction of the magnetic field vector and the plane of the slabs. As long as the magnetic field vector is confined within the cb plane (i.e., it is rotated in the plane normal to the slabs), the spin-flop transition always remains first order. However, in the ca plane (the field vector is coplanar with the slabs), the spin-flop transition is only first order within a small range of angles between the magnetic field vector and the AFM easy (c) axis ($0 < \theta < 20^\circ$). The data shown in Fig. 5 compare well to that found in CuCl$_2$·2H$_2$O, which also has an orthorhombic structure. In CuCl$_2$·2H$_2$O, the $a$ axis is the AFM easy axis, the $b$ axis is the next easiest axis (spin-flop axis), and the $c$ axis is the hard axis. The magnetization of CuCl$_2$·2H$_2$O measured as a function of $\theta$ with the magnetic field vector confined in the $ac$ plane exhibits a constant value at low $\theta$ (when $\mathbf{H}_||\mathbf{a}$) followed by a sharp drop, whereas both of these features are absent in the $ab$ plane measurements. Hence, our results for Gd$_4$Ge$_3$ are consistent with the AFM easy axis being the $c$ axis, the next easiest axis (the spin-flop axis) is the $a$ axis, and the hard axis is the $b$ axis. This means that with the occurrence of the spin-flop transition, the Gd moments that were coupled antiferromagnetically along the $c$ axis are rotated within the plane of the slab and become nearly collinear with the $a$ axis. In the cb plane measurements, the spin rotation is discontinuous because the spin-flop axis is always perpendicular to the magnetic field vector, whereas in the ca plane measurements, the spin rotation is continuous because the spin-flop axis is no longer perpendicular to the field vector.

Even though data about microscopic magnetism of $R$,$\text{Si}$,$\text{Ge}_{2-x}$ compounds with heavy lanthanides are limited to only a few representatives with $R$=Gd, Tb, and Er, the spin-flop AFM configuration of Gd$_4$Ge$_3$ with the magnetic moments coplanar with the slabs is quite reasonable. In all known cases, there is a clear tendency toward ferromagnetism of the individual slabs. Furthermore, the moments are coplanar or nearly coplanar with the slabs in compounds formed by heavy lanthanides with small orbital contribution to the total magnetic moment (Gd and Tb), while the moments become normal to the slabs in Er, where the orbital contribution dominates. We believe that this is related to a gradual reduction of the strength of the isotropic exchange interactions and to an increasing anisotropic contribution from the magnetoelastic coupling that arises from the competition between the anisotropy of the layered crystal structure and single ion anisotropy. Thus, the prediction by Levin et al., which was made without direct evidence, was correct, and the results presented above do confirm that the $a$ axis is indeed the spin-flop axis of Gd$_4$Ge$_3$.

It is worth noting that the theoretical treatment using the molecular field approximation of the phase transition between a normal AFM phase and a spin-flop AFM phase in a uniaxial antiferromagnet shows that the range of angles over which a first order spin-flop transition may be observed is quite small because the anisotropy energy is usually small compared to the isotropic exchange energy. This conclusion is in agreement with some other uniaxial antiferromagnets, where the maximum tilt angle at which a first order spin-flop transition between the AFM easy axis and the spin-flop axis can be observed ($\theta_{\text{max}}$) has a magnitude of less than $1^\circ$. This is indeed much smaller than the value of $\theta_{\text{max}}$ = $20^\circ \pm 5^\circ$ seen in Gd$_4$Ge$_3$, especially considering the possible misalignment of the field vector with respect to the crystallographic direction(s). As pointed out by Rohrer and Thomas, the maximum tilt angle can be expressed as $\theta_{\text{max}}=28.6^\circ \times H_{\text{an}}/H_{\text{ex}}$ when $K_1=0$. Here, $K_1$ is the anisotropy constant between the two sublattices, and $H_{\text{an}}$ and $H_{\text{ex}}$ are the anisotropy and exchange fields, respectively. This indicates that although the isotropic exchange interactions are
always dominant in uniaxial antiferromagnets, the value of $H_{an}/H_{ex}$ is large in Gd$_5$Ge$_4$ when compared to some other transition metal systems, thus leading to a relatively large $\theta_{\text{max}}$.

The unusually large $H_{an}/H_{ex}$ is a reflection of the fact that anisotropic exchange interactions in Gd$_5$Ge$_4$ are stronger than in many other Gd-based systems. The magnetic anisotropy of the title compound is probably dominated by the anisotropic exchange interactions due to its distinctly layered and, therefore, anisotropic orthorhombic crystal structure. This behavior is similar to that observed in GdRu$_2$Si$_2$ and GdRu$_2$Ge$_2$, where the low temperature anisotropy may originate from anisotropic exchange interactions caused by the anisotropy of the tetragonal lattice. Anisotropic exchange interactions are also a likely origin of the anisotropy observed in GdCu$_2$, where a model based on the classical dipole-dipole exchange fails to describe the easy magnetization direction in this non-collinear amplitude-modulated magnetic structure, even though this model works well for other Gd-based compounds, e.g., GdAg, GdAu$_2$Si$_2$, and GdCu$_2$In.

CONCLUSIONS

The angular dependence of the spin-flop transition in single crystal Gd$_5$Ge$_4$ has been investigated by magnetization measurements. When the magnetic field vector is tilted away from the antiferromagnetic easy axis (c axis) toward the b axis, a first order spin-flop transition is observed over a wide range of tilt angles $0 < \theta < 0.5^\circ$. However, when the field vector is tilted away from the c axis toward the a axis, the first order spin-flop transition is only observed over a small range of tilt angles ($0 < \theta < 20^\circ$). When $\theta$ exceeds $20^\circ$, the spin-flop transition becomes a second order transformation, suggesting that in the spin-flop AFM phase, the Gd moments are antiferromagnetically coupled along the a axis.

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