Structural, magnetothermal, and magnetotransport properties of single crystal Tb$_5$Si$_2.2$Ge$_1.8$ and spontaneous generation of voltage in single crystal Gd$_5$Si$_2$Ge$_2$ and Gd

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Structural, magnetothermal, and magnetotransport properties of single crystal \( \text{ Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) and spontaneous generation of voltage in single crystal \( \text{ Gd}_5\text{Si}_2\text{Ge}_2 \) and Gd

by

Min Zou

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ABSTRACT
A systematic study of single crystalline \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \), including magnetic field induced crystallographic and magnetic phase transformations, magnetocaloric effect, ferromagnetic short-range correlations, electrical resistivity, magnetoresistance, and spontaneous generation of voltage (SGV) has been presented. A study of SGV in single crystalline \( \text{Gd}_5\text{Si}_2\text{Ge}_2 \) and \( \text{Gd} \) has also been included.

The metamagnetic-like transitions and giant magnetocaloric effect were observed with the magnetic field applied parallel to the \( a \)- and \( c \)-axes, but not the \( b \)-axis in a \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) single crystal. The \textit{in-situ} x-ray powder diffraction study indicates that these metamagnetic-like transitions are coupled to a crystallographic phase transformation occurring \textit{via} strong magnetoelastic interactions. The magnetocrystalline anisotropy plays an important role in this system. Magnetic fields less than 40 kOe can not drive either the magnetic or the crystallographic phase transition to completion for \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) powder due to the strong single ion anisotropy of \( \text{Tb} \).

Magnetic field dependencies of the critical temperatures of magnetic phase transitions of \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) are highly anisotropic for both the main magnetic ordering process occurring around 120 K and a spin reorientation transition at \( \approx 70 \) K. Magnetic-field-induced phase transitions occur with the magnetic field applied isothermally along the \( a \)-and \( b \)-axes (but not along the \( c \)-axis) between 1.8 and 70 K in fields below 70 kOe. Strongly anisotropic thermal irreversibility is observed in the Griffiths phase regime between 120 and 200 K with applied fields ranging from 10 to 1000 Oe. Our data: (1) show that the magnetic and structural phase transitions around 120 K are narrowly decoupled; (2) uncover the anisotropy of ferromagnetic short-range order in the Griffiths phase; and (3) reveal some unusual magnetic domain effects in the long-range ordered state of the \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) compound. The temperature-magnetic field
phase diagrams with field applied along the three major crystallographic directions have been constructed.

The positive colossal magnetoresistance (CMR) with a magnitude of ~150% was observed with the magnetic field applied parallel to the $a$-axis, but not the $b$- and $c$-axes in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystals. The electrical resistivity shows a low-temperature high-resistivity behavior (i.e. the resistivity at low temperature is higher after the transformation to the low temperature phase than the resistivity of the phase before the transition) along the $a$-axis, contrary to those along the $b$- and $c$-axes. The positive CMR effect originates from an intrinsic crystallographic phase coexistence state frozen below the Curie Temperature ($T_C$). The differences in the temperature dependencies of electrical resistivities and longitudinal magnetoresistance along the $a$-axis and those along the $b$- and $c$-axes can be explained by the geometry of the phase boundaries at low temperatures, and the inability of the external magnetic field to induce the crystallographic phase transformation along the $b$- and $c$-axes.

Temperature-induced SGVs were observed along all three principal crystallographic axes of Tb$_5$Si$_{2.2}$Ge$_{1.8}$, but not in Gd. Field-induced SGVs were observed with magnetic fields less than 40 kOe applied along the $a$-axis of Tb$_5$Si$_{2.2}$Ge$_{1.8}$, and the $c$-axis of Gd. The absence of the temperature induced SGV in Gd indicates the key role first-order phase transformations play in the appearance of the effect when temperature varies. The anisotropy of magnetic field induced SGV in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ and the existence of field induced SGV in Gd, highlight the importance of the magnetocaloric effect in bringing about the SGV. In single crystal and polycrystalline Gd$_5$Si$_2$Ge$_2$ during the coupled magneto-structural transformations, reversible and repeatable SGV responses of the materials to the temperature and magnetic field have been observed. The parameters of the response and the magnitude of the signal are anisotropic and rate dependent.
The magnitude of the SGV signal, and the critical temperatures and critical magnetic fields at which the SGV occurs vary with the rate of temperature and magnetic field changes.
CHAPTER 1. Introduction

Rare earth intermetallic compounds $R_5(Si_xGe_{1-x})_4$, where $R$ are lanthanides, were first
discovered in 1966 by Smith et al.\textsuperscript{1,2} The renewed interest in $R_5(Si_xGe_{1-x})_4$ started from the
discovery of the giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ in 1997.\textsuperscript{3,4} Other
extraordinary physical properties, such as the colossal magnetostriction,\textsuperscript{5-8} giant
magnetoresistance (GMR),\textsuperscript{9-16} and spontaneous generation of voltage\textsuperscript{17} (SGV) were
discovered soon after.

Most of the research on $R_5(Si_xGe_{1-x})_4$ commenced from $Gd_5(Si_xGe_{1-x})_4$, which is quite
representative in this family. An introduction to the $Gd_5(Si_xGe_{1-x})_4$ system about its
crystallography, magnetism, and extraordinary physical properties is presented first. It is
followed by an introduction to the $Tb_5(Si_xGe_{1-x})_4$ system because one of the major
compounds under investigation in this thesis is $Tb_5Si_{2.2}Ge_{1.8}$. An introduction to the
magnetocaloric effect, giant magnetoresistance, thermoelectric power, and Griffith’s phase in
general, all of which are closely relevant to this thesis study, is included thereafter. Finally,
the motivations of this thesis study and the thesis organization are presented at the end of this
Chapter.

1.1. Crystallography, magnetism and physical properties of $Gd_5(Si_xGe_{1-x})_4$

As shown in Figure 1.1, the $Gd_5(Si_xGe_{1-x})_4$ compounds have layered structures.\textsuperscript{18} Their
building blocks are essentially equivalent sub-nanometer thick two-dimensional slabs, which
are composed of cubooctahedra $[Gd_3T_{10/3}]$ and double trigonal prisms $[Gd_2T_{2/3}]$, where $T =
Si, Ge$.\textsuperscript{19,20,21} The $T – T$ covalent-like bonds between these slabs determine the crystal
structure and the type of magnetic ordering.
Three types of crystal structures exist in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$. The first one is the Gd$_5$Si$_4$-type structure [Figure 1.1(c)], where the inter-slab T – T atomic distances are 2.5–2.6 Å. The crystal structure is orthorhombic with space group Pnma, so it is also known as the O(I) phase. It orders ferromagnetically at low temperatures and then transforms to a paramagnet upon heating without changing its crystal structure. The second one is the Gd$_5$(Si$_2$Ge$_2$)-type structure [Figure 1.1(b)], where half of the inter-slab T – T distances remain ~2.6 Å and another half expand to ~3.5 Å. The crystal structure is monoclinic (also named as the M phase) with the space group P112$_1$/a. This structure is stable only in the paramagnetic (PM) state. The third one is the Sm$_5$Ge$_4$-type structure [Figure 1.1(a)]. Its crystal structure is also orthorhombic with the same symmetry, Pnma, as that of the O(I) phase. But all the inter-slab T – T distances expand to 3.6 Å in the Sm$_5$Ge$_4$-type structure, so it is also known as the O(II) phase to distinguish it from the O(I) phase. The Sm$_5$Ge$_4$-type phase supports antiferromagnetic (AFM) and PM states at low and high temperatures, respectively.

The atomic radii of Si and Ge atoms in tetrahedral covalent bonds are 1.17 and 1.22 Å, respectively. Hence, when the T – T atomic distance is 2.5–2.6 Å, the bonds between them...
are regarded as covalent-like. On the other hand, when the distance expands to 3.5–3.6 Å, the covalent-like bonds are considered broken.

Figure 1.2 shows the magnetic and crystallographic phase diagram of Gd₅(SiₓGe₁₋ₓ)₄. The Gd₅Si₄-type structure [O(I) phase] exists over the whole composition range at low temperatures and is ferromagnetically ordered. In the Si-rich region with 0.507 ≤ x ≤ 1, it transforms from a ferromagnetic (FM) to a PM state above 300K, without the change in crystal structure.

The Gd₅Si₂Ge₂-type structure (M phase) exists in the intermediate composition range when 0.4 < x ≤ 0.503. It is a distortion of the O(I) structure by shear displacements of the slabs by 0.2 Å along the a-axis. The transformation between the M and O(I) phases is accompanied by a simultaneous magnetic phase transition between the FM and PM states. It is, therefore, called a coupled magnetostructural phase transformation.
The Sm$_3$Ge$_4$-type structure [O(II) phase] exists in the Ge-rich region when $0 < x \leq 0.3$. The O(II) phase exists in the AFM and PM states at low and high temperatures, respectively. The transformation between O(I) and O(II) phase is also a coupled magnetostructural phase transition.

The compounds within the range of compositions of $0.503 < x < 0.575$ and $0.3 < x \leq 0.4$ contain two phases from their adjacent single-phase regions.

The magnetic structures of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, remain undetermined because of a tremendous neutron absorption cross section of the naturally occurring mixture of Gd isotopes. The only exception is Gd$_5$Ge$_4$, the magnetic structure of which has been determined using resonant x-ray magnetic scattering.\textsuperscript{23}

Numerous extraordinary strong effects occur during first-order coupled crystallographic and magnetic phase transformations in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$.\textsuperscript{19} These are between the M/PM and O(I)/FM phases when $0.4 < x \leq 0.503$, and between the O(I)/FM and O(II)/AFM when $0 < x \leq 0.3$. The coupling of the crystallographic and magnetic phase transformations is evident from the concurrent change of the magnetization and crystal structure observed in Gd$_5$Ge$_4$ and related materials through bulk magnetization and in-situ x-ray powder diffraction studies.\textsuperscript{24,25} They can be triggered by either varying temperature,\textsuperscript{21} magnetic field,\textsuperscript{5,26} or hydrostatic pressure.\textsuperscript{27,28}

The Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ compounds exhibit magnetocaloric effects that are 2 to 4 times greater than ordinary magnetic solids.\textsuperscript{3,4} For the majority of magnetic materials, the MCE comes only from the magnetic entropy change during their magnetic order-disorder transitions. In Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, the accompanying crystallographic phase transformation gives rise to a
remarkably strong additional contribution arising from the difference of the entropies of two crystallographic modifications, thus resulting in the GMCE.\textsuperscript{4,29}

The magnetostriction ($\lambda = \Delta l/l$) of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ reaches $10^{-3}$ in low magnetic fields.\textsuperscript{5-8} It is therefore colossal compared to normal $\lambda = 10^{-5} \sim 10^{-6}$ (Ref. 30). The colossal magnetostriction is due to the capability of the magnetic field to trigger the crystallographic phase transformation that involves a $\sim 1\%$ unit cell volume change.

The magnetostriction of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ varies between 10% and 50% for different compositions during the magnetic field induced magnetostructural phase transformations.\textsuperscript{9-16} It is much greater than the same in conventional magnetic materials, and is of the same order of magnitude as observed in artificially fabricated GMR multilayers.\textsuperscript{31} In general, the electrical resistance is lower in O(I)/FM phase compared to its high-temperature/low-magnetic-field phases. With $0.4 < x \leq 0.503$, the higher electrical resistance in the M/PM phase is due to a stronger magnon scattering, a twinned microstructure, and a change of electronic velocity at the Fermi level.\textsuperscript{16,21} When $0 < x \leq 0.3$, different density of states at the Fermi level due to a change of band structure from O(I) to O(II) phase together with stronger magnon scatterings in the AFM state were suggested to be responsible for the -50% GMR.\textsuperscript{14}

Voltages of tens of microvolts are generated spontaneously across Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ specimens that are a few millimeters long when they undergo magnetostructural transformations.\textsuperscript{17} Since during measurements no current is supplied to the specimens, this phenomenon is regarded as a spontaneous generation of voltage (SGV). The SGV is especially intriguing because it may result in development of sensors, which can respond not only to changes in temperature, pressure, and/or magnetic field, but most importantly to the rates of their changes without the
need for a complicated analysis of signals. Furthermore, all of these can be done by a single sensor requiring no standby power.

1.2. Crystallography, magnetism and physical properties of Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$

The Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ system is the second most studied subset in the family of R$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys. The original crystallographic and magnetic phase diagram (Figure 1.3) was established in 2002.$^{32}$

Similar to Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ system also accommodates three types of crystallographic structures, which are O(I), O(II), and M. The difference between Tb$^{3+}$ and Gd$^{3+}$ ions, however, brings about three major differences between Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ and Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ systems. First, in Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ when $0 < x \leq 0.3$, the O(II)/AFM phase does not transform to O(I)/FM phase at low temperature as is the case in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ when $0 < x \leq 0.3$. The O(II)/AFM Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ transforms to another AFM state and retains its O(I) structure. Second, after transforming from M/PM and O(I)/PM to O(I)/FM when $0 < x \leq 0.3$ and $0.35 < x \leq 1$, respectively, Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ undergoes a spin reorientation transition to another FM phase. This does not occur in the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ system. Third, the crystallographic phase transformation between O(I) and M structures and magnetic order-disorder phase transition between FM and PM states in Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ are decoupled by $\sim 10$ K when $x = 0.5$. $^{33}$ On the contrary, the magnetic and crystallographic phase transformations in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ are always coupled. In Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$, the two (crystallographic and magnetic) transformations, however, can be recoupled by applying hydrostatic pressures greater than 8.6 kbar.$^{34}$
Complex magnetic structures have been observed in Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ by means of neutron powder and single crystal diffraction.\textsuperscript{32,35} The magnetic moments are mainly confined to the $ac$ plane. In Tb$_5$Ge$_4$, the moments are in a canted AFM configuration with the $c$-axis as the main AFM axis. The Tb atoms in three inequivalent crystallographic sites make different canting angles with the $c$-axis. The canting angles change with temperature, and thus lead to a spin reorientation transition between two AFM phases at $T_{SR} = 55$ K. The angles of the Tb1 (4$c$ site), Tb2 (8$d$ site), and Tb3 (8$d$ site) moments with the $c$-axis are 10°, 23°, and 31° at 2 K, and 0°, 7°, and 27° at 85 K. While all the Tb1 moments are in the $ac$ plane, the AFM coupled $b$-axis components are composed of 19% to 7% of the total Tb2 moments, and 21% to 27% of the total Tb3 moments from 2 to 85 K.

The moments become canted FM in the intermediate compositional range when $x = 0.5, 0.55, 0.6$ and 0.625. The $a$-axis is the easy magnetization direction. A spin reorientation transition occurs between two canted FM phases at $T_{SR} = 70$ or 75 K for $x = 0.5$ or 0.55, respectively. The arrangement of the $c$-axis components changes from AFM to FM upon cooling through
This corresponds to an increase of the canting angles with the $a$-axis, and a decrease of the $a$-axis components of the moments. For example, in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ ($x = 0.55$), the canting angles of the Tb1, Tb2, and Tb3 moments with the $a$-axis are 35.6°, 47.8°, and 30.5° at 4.2 K; and 1.3°, 19.6°, and 3.1° at $T_{SR} = 75$ K, respectively. No Tb1 moment has $b$-axis component. Two models have been proposed for magnetic structure of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ below 75 K. For Tb2 and Tb3 at 4.2 K, the AFM $b$-axis components are composed of 25% and 34% of Tb2, and 23% and 13% of Tb3 moments for model 1 and 2, respectively. At 75 K, the AFM $b$-axis components of Tb2 and Tb3 are 25% and 3%, respectively. The crystal and magnetic structures of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is shown in Figure 1.4.

The magnetic structure of Tb$_5$Si$_4$ is similar to those of intermediate compositional range compounds except for the slight variation of the directions of magnetic moments. A spin reorientation transition occurs at $T_{SR} = 80$ K between two canted FM phases. The average canting angles of Tb1, Tb2, and Tb3 moments with the $a$-axis change from 33°, 50°, and 34° at 2 K to 3°, 17°, and 4° at 85 K. The ordering of $c$-axis components changes from AFM to FM upon cooling through $T_{SR}$. No Tb1 moment components appear in the $b$-axis direction. The AFM coupled $b$-axis components of Tb3 is almost negligible, constituting 3% to 1% of

![Figure 1.4. Crystal and magnetic structures of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ following Ref. 35. The left panel shows the magnetic structure between 75 and ~120 K and it also highlights the connectivity of the slabs via -Tb1-T3-T3-Tb1- bonds. The top panel on the right shows the orientations of the magnetic moments of the Tb atoms in one slab between 75 and ~120 K. The bottom panel on the right shows the orientations of the magnetic moments in one slab below 75 K. T1, T2 and T3 represent a statistical mixture of Si and Ge atoms of the 2.2:1.8 (0.55:0.45) atomic ratio.](image-url)
the total moments from 2 to 85 K. The AFM coupled \( b \)-axis components of Tb2 moments are 23% and 16% of the total moments at 2 and 85 K, respectively.

The GMCE of \( \text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) is observed in the intermediate compositional range when \( 0.35 < x < 0.65 \),\(^{36-38}\) where a first-order transformation between the O(I) and M structures occurs. The magnetic entropy change (\( \Delta S_M \)) of \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) upon \( \Delta H = 50 \text{ kOe} \) is 21.8 J/kg K, which is comparable to that of \( \text{Gd}_5\text{Si}_2\text{Ge}_2 \).\(^3,36\) A further 40% increase of \( \Delta S_M \) of \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) is achieved by applying hydrostatic pressures, which recouples the crystallographic and magnetic transformations.\(^34\)

The colossal magnetostriction is also observed in polycrystalline \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) with \( \lambda_{\text{max}} = \Delta l/l = -1.2 \times 10^{-3} \).\(^32\) A large anisotropy between parallel (\( \lambda_{||} \)) and perpendicular (\( \lambda_{\perp} \)) components of the magnetostriction in \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) indicates an active role of the highly anisotropic \( \text{Tb}^{3+} \) ions.

The electrical resistivity as a function of temperature and magnetic field of \( \text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4 \), has been studied for the compositions with \( x = 0.5, 0.6, 0.75, \) and 1 by different research groups using polycrystalline samples.\(^{32,33,39,40}\) No abrupt changes of the electrical resistivities of \( \text{Tb}_5\text{Si}_3\text{Ge} (x = 0.75) \) and \( \text{Tb}_5\text{Si}_4 (x = 0) \) compounds was observed between 10 and 300 K, in agreement with the crystallographic study of these compounds showing no crystallographic phase transformation over this temperature range.\(^33\) Polycrystalline \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) sample exhibit a sharp 30% increase of the electrical resistivity at the crystallographic phase transformation temperature upon heating, and a negative magnetoresistance,\(^34\) similar to those observed in \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) with \( x = 0.1, 0.45 \) and 0.5 (Refs. 9,10,14). The magnetoresistance of the \( \text{Tb}_5\text{Si}_2\text{Ge}_2 \) compound, however, does not show a metamagnetic transition as was observed in the closely related compound with Gd. The magnitude of the magnetoresistance is substantially smaller than that in the latter. This
phenomenon was explained by an approximately 10 K decoupling of the magnetic and crystallographic phase transformations in the Tb$_5$Si$_2$Ge$_2$ compound, leading to an incomplete magnetic-field-induced magnetic phase transition.\textsuperscript{34} Interestingly, a polycrystalline sample of Tb$_5$Si$_{2.4}$Ge$_{1.6}$ shows a distinctly different electrical resistivity behavior at its crystallographic phase transformation, \textit{i.e.} an abrupt 40\% drop of the electrical resistivity upon heating.\textsuperscript{40} Thus, this compound appears to have a low-temperature high-resistivity behavior rather than a low-temperature low-resistivity one as observed in other Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ compounds.

1.3. The magnetocaloric effect (MCE)

First discovered in 1881,\textsuperscript{41} the magnetocaloric effect (MCE) is a magnetothermal effect that manifests as an adiabatic temperature change ($\Delta T_a$) of a magnetic solid when subjected to an applied magnetic field. The phenomenon is in the foundation of magnetic refrigeration technology.

For a rare earth magnetic material at constant pressure, the total entropy is the sum of magnetic, lattice, and electronic entropies ($S_M$, $S_L$, and $S_E$, respectively).

$$S = S_L + S_E + S_M$$

(1)

Applying a magnetic field decreases the disorder of magnetic moments, thus decreasing $S_M$. During an adiabatic process, total entropy remains constant. The decrease of $S_M$ is compensated by the equivalent increase of $S_L$ and $S_E$, which leads to the increase of temperature of the material. This is known as heating by adiabatic magnetization. Conversely, the process of cooling by adiabatic demagnetization causes a temperature decrease of the material by removal of the external magnetic field.

The differential of $S(H, T)$ can be written as:
\[ dS(H,T) = d(S_L(H,T) + S_E(H,T) + S_M(H,T)) \]
\[ = \left( \frac{\partial S_L(H,T)}{\partial T} \right)_H dT + \left( \frac{\partial S_L(H,T)}{\partial H} \right)_T dH + \left( \frac{\partial S_E(H,T)}{\partial T} \right)_H dT + \left( \frac{\partial S_E(H,T)}{\partial H} \right)_T dH \]
\[ + \left( \frac{\partial S_M(H,T)}{\partial T} \right)_H dT + \left( \frac{\partial S_M(H,T)}{\partial H} \right)_T dH \]

\[ (2) \]

According to the second law of thermodynamics and the definition of heat capacity at constant parameter \( x \), equation (2) can be written as:

\[ dS(H,T) = \frac{C_L(T)}{T} dT + \frac{C_E(T)}{T} dT + \frac{C_M(T)}{T} dT + \left( \frac{\partial S_M(H,T)}{\partial H} \right)_T dH \]

\[ (3) \]

where \( C_L(T) \), \( C_E(T) \), and \( C_M(T) \) are lattice, electronic, and magnetic parts of the total heat capacity of the material.

The differential of the magnetic entropy \( S_M \) is the sum of the last two terms of equation (3):

\[ dS_M(H,T) = \frac{C_H(T)}{T} dT + \left( \frac{\partial S_M(H,T)}{\partial H} \right)_T dH \]

\[ (4) \]

According to Maxwell relation:

\[ \left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H \]

\[ (5) \]

Equation (15) can be written as:

\[ dS_M(H,T) = \frac{C_H(T)}{T} dT + \left( \frac{\partial M}{\partial T} \right)_H dH \]

\[ (6) \]

For a finite temperature and magnetic field change, \( \Delta T \) and \( \Delta H \), the magnetic entropy change \( \Delta S \):
\( \Delta S_M(H, T) = S_M(H + \Delta H, T + \Delta T) - S_M(H, T) = \)

\[
= \int_{H}^{H+\Delta H} \left( \frac{\partial M(H, T + \Delta T)}{\partial T} \right)_{H} dH + \int_{T}^{T+\Delta T} \frac{C(H, T)}{T} dT \quad (7)
\]

During an isothermal magnetization process,

\[
\Delta H = H_2 - H_1 \quad (H_2 \text{ is the final and } H_1 \text{ is the initial magnetic field})
\]

\[
\Delta T = 0, \quad \text{and} \quad \int_{T}^{T+\Delta T} \frac{C(H, T)}{T} dT = 0
\]

Assuming that the lattice and electronic entropies are not affected by \( H \), the total entropy change:

\[
\Delta S(H, T) = \Delta S_M(H, T) = \int_{H}^{H+\Delta H} \left( \frac{\partial M(H, T + \Delta T)}{\partial T} \right)_{H} dH = \int_{H_1}^{H_2} \left( \frac{\partial M(H, T)}{\partial T} \right)_{H} dH \quad (8)
\]

Therefore, the total entropy change during an isothermal process can be obtained through magnetization data.

During an adiabatic magnetization process, the total entropy of the material remains constant, following equation (2):

\[
dS(H, T) = \frac{C_L(T)}{T} dT + \frac{C_E(T)}{T} dT + \frac{C_M(T)}{T} dT + \left( \frac{\partial S_M(H, T)}{\partial H} \right)_T dH = 0 \quad (9)
\]

\[
\frac{C_L(T)}{T} dT + \frac{C_E(T)}{T} dT = - \left( \frac{C_H(T)}{T} dT + \left( \frac{\partial S_M(H, T)}{\partial H} \right)_T dH \right) \quad (10)
\]

therefore,

\[
dT(T, H) = - \frac{T}{\left( C_L(T, H) + C_E(T, H) + C_M(T, H) \right) \left( \frac{\partial S_M(H, T)}{\partial H} \right)_T} dH \quad (11)
\]
Substituting the total heat capacity \( C = C_L + C_E + C_M \) into equation (11), and using equation (5), we get:

\[
dT(T, H) = -\frac{T}{C(T, H)} \left( \frac{\partial S_m(H, T)}{\partial H} \right)_T dH = -\frac{T}{C(T, H)} \left( \frac{\partial M(H, T)}{\partial T} \right)_H dH
\]

(12)

Therefore, under an adiabatic magnetization process from \( H_1 \) to \( H_2 \), the temperatures change of the material is:

\[
\Delta T_{ad}(T, \Delta H) = -\int_{H_1}^{H_2} \frac{T}{C(T, H)} \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH
\]

(13)

From the first part of equation (12), one can also derive the magnetic entropy change by heat capacity data:

\[
\Delta S_m(T, \Delta H) = \int_0^{\Delta H} \left( C(T, H) \right)_{H_2} - C(T, H)_{H_1} \right) dT
\]

(14)

1.4. The magnetoresistance

The magnetoresistance (MR) is the change of electrical resistivity of a material when subjected to an applied magnetic field. It is generally defined as

\[
MR = \frac{\rho(H) - \rho(0)}{\rho(0)}
\]

where \( \rho(H) \) and \( \rho(0) \) represent the electrical resistivities with and without the applied magnetic field, \( H \), respectively. Although some researchers define as

\[
MR = \frac{\rho(H) - \rho(0)}{\rho(H)}
\]

in this thesis, the
MR = \frac{\rho(H) - \rho(0)}{\rho(0)} is used.

The magnetoresistance is differentiated as longitudinal or transverse magnetoresistance when
the applied magnetic and electric fields are parallel or perpendicular to each other,
respectively.

The magnetic field changes the path of conduction electrons due to the Lorentz force. The
conduction electrons therefore experience difference scattering processes, resulting in the
magnetoresistance. The pathway of conduction electrons between scatterings changes from
linear to helical upon the applied magnetic field. This gives rise to a positive MR, i.e. a
higher resistivity of the material upon application of magnetic field.\(^\text{42}\)

For a ferromagnetic material, an applied magnetic field typically decreases the randomness of
the orientation of magnetic moments, thus decreasing the scattering of conduction electrons
by magnons, resulting in a negative MR with a magnitude of a few percent. Some magnetic
multilayers, such as Fe/Cr with the thickness of Fe and Cr layers of 3 and 0.9 nm,
respectively, show magnetoresistance up to 40 to 50\%.\(^\text{43}\) This is called giant
magnetoresistance (GMR), and it originates from spin dependent scattering.\(^\text{44}\) The magnetic
thin layers are coupled antiferromagnetically in a zero magnetic field. When magnetic field
aligns the layers into a ferromagnetic state, the electrical resistivity drops abruptly. The
discovery of the GMR effect has lead to a revolutionary impact on data storage industry; and
the scientists who discovered the effect in 1988 won the 2007 Nobel Prize.\(^\text{45}\)

The search for new materials with greater MR led to the discovery of the colossal
magnetoresistance (CMR) effect in 1994.\(^\text{46}\) Doped manganites with a general formula of
\(A_{1-x}B_x\text{MnO}_3\), where \(A\) is La or Nd and \(B\) is Ba, Sr, Ca, or Pb, with \(x\) around 0.33, exhibit a
~100% negative MR. The interplay among spin, charge, orbital, and lattice degrees of freedom leads to the coexistence of large domains of charge-ordered insulating and charge disordered metallic phases in these compounds. Hence, these phases have nearly equal free energy. A magnetic field, therefore, can effectively alter the energy landscape by spin-lattice coupling, in turn causing percolation of conducting paths and transforming the compounds to metallic phases.

In addition to GMR multilayers and doped manganites, large MR effects have been reported in pyrochlore Tl$_2$Mn$_2$O$_7$, Cr-based chalcogenide spinels, Eu-based hexaboride, doped silver chalcogenides, naturally layered LaMn$_2$Ge$_2$, semimetallic Bi nanowire arrays, semiconducting InN film, GaAs/(AlGa)As, and Co-doped FeSb$_2$. For those compounds that exhibit negative GMR or CMR, spin dependent scattering is the underlying mechanism. For materials exhibiting positive CMR effect, the mechanisms were believed to be quantum interference effects, band splitting effects, or they were left without a feasible explanation.

1.5. The Griffiths phase

Robert B. Griffiths proposed in 1969 (Ref. 56) that for a random Ising ferromagnet the magnetization may become a non-analytical function of magnetic field $H$ at temperatures below the long-range ordering temperature of a regular Ising ferromagnet. In a regular Ising ferromagnet, all lattice sites are occupied by Ising spins (either up or down). The exchange interactions exist between the nearest-neighbor spins. In a random Ising ferromagnet, Ising spins only occupy a fraction, $p$, of the lattice sites. The exchange interactions exist between spins on neighboring pairs of occupied sites. The occupancy probability $p$ of a lattice site does not depend on magnetic field, temperature, and the occupancy of other sites. The
Griffiths phase is defined as a random Ising ferromagnet when $T_C < T < T_G$, where $T_G$ and $T_C$ are the critical temperatures of the onset of magnetic long-range order of the regular ($p = 1$) and the random ($0 < p < 1$) systems, respectively.\textsuperscript{57} This definition has further been extended to a random magnetic system when $T_C < T < T_G$, where a random magnetic system can be specified by a particular bond probability distribution, $T_C$ is its particular ordering temperature, and $T_G$ is the highest ordering temperature allowed by the distribution. For unbounded distributions $T_G = \infty$.\textsuperscript{58}

The Griffiths theorem has attracted much attention because it may help in understanding of cooperative phenomena in a fully occupied lattice, solving problems involving substitutonal defects in regular crystal lattices, and detecting the validity of approximate theory.\textsuperscript{59-62} Experimental observations of Griffiths phase, although predicted to be extremely remote by some theorists in 1970’s,\textsuperscript{62} were reported much later than theoretical studies. A field-induced Griffiths phase was observed in FeCl\textsubscript{2}, which is manifested as domainlike antiferromagnetic correlations in paramagnetic state.\textsuperscript{63} Later, the existence of the Griffiths phase was reported in non-fermi-liquid $f$-electron compounds.

Initial experimental evidence is a less than unity exponent $\lambda$ obtained by fitting the expression relating the specific heat $C$ to the static magnetic susceptibility $\chi$, given by $C(T)/T \propto \chi(T) \propto T^{-1+\lambda}$.\textsuperscript{64,65} The coexistence of a metallic paramagnetic phase with a granular magnetic phase in non-Fermi liquid $f$-electron compounds, such as Th\textsubscript{1-x}U\textsubscript{x}Pd\textsubscript{2}Al\textsubscript{3}, Y\textsubscript{1-x}U\textsubscript{x}Pd\textsubscript{3}, and UC\textsubscript{5-x}M\textsubscript{x} ($M = \text{Pd, Pt}$), was believed to be equivalent to the Griffiths phase of dilute magnetic system.\textsuperscript{64} The Griffiths phase was also observed in CMR La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3}, La\textsubscript{0.66}(Pb,Ca)\textsubscript{0.34}MnO\textsubscript{3}, paramagnetic La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}, La\textsubscript{0.7}Ba\textsubscript{0.3}MnO\textsubscript{3}, itinerant magnetic
semiconductor Fe$_{1-x}$Co$_x$S$_2$, Sm$_{1-x}$Ca$_x$MnO$_3$ (0.80 ≤ x ≤ 0.92). It was claimed that “Colossal Magnetoresistance is a Griffiths Singularity”.

1.6. Motivations of the study and thesis organization

To better understand the relationships between the magnetism and crystallography in the Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ system, and the origin of the large magnetocaloric effect, dc magnetization and in-situ x-ray powder diffraction studies of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ have been conducted. Both single crystal and powered specimens were examined in the vicinity of $T_C$ to seek structure-property information, fine details of which may be masked by random orientation of the grains in polycrystalline samples. The results are presented in Chapter 3.

The decoupling of the magnetic and structural phase transitions in Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ leads to a complicated crystallographic and magnetic phase coexistence near $T_C$. Furthermore, intrinsic twinning at the nanoscale in the monoclinic phase enhances the Griffiths-like phase behavior in polycrystalline Tb$_5$Si$_2$Ge$_2$, which is detected by the less than unity exponent of the inverse susceptibility in magnetic fields between 1 and 1500 Oe due to ferromagnetic short-range order. Anisotropic ferromagnetic short-range order has been observed in both antiferromagnetic and paramagnetic states of single crystal Gd$_5$Ge$_4$, and was ascribed to the anisotropy of the layered crystal structure of the Gd$_5$Ge$_4$ compound considering negligible single ion anisotropy of Gd$^{3+}$. The anisotropy is expected to be much enhanced when R = Tb. To carry out a systematic study of the magnetization of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound and to further explore the anisotropy of the Griffiths phase behavior, the temperature and magnetic field dependencies of the dc magnetization along the three principal crystallographic axes of a high purity Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal are presented in Chapter 4.
It has been established that phase coexistence states play a key role in the colossal magnetoresistance (CMR) effects of the perovskite manganites, and theoretical studies of them have suggested that (i) the CMR effect is a Griffiths singularity;\(^{66}\) and (ii) colossal effects should be ubiquitously accompanied by competition between ordered phases.\(^{77}\)

Crystallographic phase coexistence phenomenon has been observed in the polycrystalline Tb\(_5\)Si\(_2\)Ge\(_2\) and Dy\(_5\)Si\(_3\)Ge compounds as well.\(^{75,78}\) It appears to be intrinsic to the R\(_5\)(Si\(_x\)Ge\(_{1-x}\))\(_4\) family due to a competition among different magnetic and crystallographic phases and thermodynamic energy scales. Thus, the magnetic energy favors an orthorhombic crystal structure at low temperatures; but the thermal energy favors a low-temperature monoclinic state. Moreover, this competition is also the foundation of the observed Griffiths-phase-like behavior in a polycrystalline Tb\(_5\)Si\(_2\)Ge\(_2\) sample.\(^{75}\)

Considering this scenario, it is imperative to conduct further study of the phase coexistence and magnetoresistance phenomena in Tb\(_5\)(Si\(_x\)Ge\(_{1-x}\))\(_4\) compounds. An electrical resistivity study of high purity Tb\(_5\)Si\(_{2.2}\)Ge\(_{1.8}\) single crystals as a function of temperature, magnetic field, and crystallographic directions is presented in Chapter 5.

A study of the SGV during the first-order phase transition in several single crystal Gd\(_5\)Si\(_2\)Ge\(_2\), Tb\(_5\)Si\(_{2.2}\)Ge\(_{1.8}\), and Gd samples is presented in Chapter 6. In addition to the SGV behavior as a function of temperature and magnetic field, the anisotropy of the signal and its dependence on the variable rates of change of these stimuli are reported.

Chapter 1 is an introduction of the research subjects with an emphasis on the literature review. Chapter 7 is comprised of general conclusions of the studies.

Most of the results presented in this thesis have been already published, accepted for publication, and one manuscript is in the final stages of revision. The results presented in
Chapter 3 were published in Physical Review B volume 75 page 024418/1-8 in 2007. The results presented in Chapter 4 were published in Physical Review B volume 78 page 014435/1-9 in 2008. The results presented in Chapter 5 are in the final stages of revision. The results on Gd$_5$Si$_2$Ge$_2$ presented in Chapter 6 were published in the Journal of Applied Physics volume 99 page 08B304 in 2006. The paper including the results on SGV in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ and Gd in Chapter 6 has been accepted for publication in the Journal of Alloys and Compounds. Reprints of published papers are included in the Appendix of this thesis.
CHAPTER 2. Experimental Techniques

2.1. Single crystal growth methods and sample description

The Gd$_5$Si$_2$Ge$_2$ and Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystals were grown by my (our) colleagues at the Ames Laboratory using the Bridgman and tri-arc methods. The Gd and Tb were prepared by the Materials Preparation Center at the Ames Laboratory. The Gd contained the following major impurities (in ppm at.): O, 440; C, 200; H, 160; N, 90; Fe, 40; and F, 30; thus it was approximately 99.9 at.% (99.988 wt.%) pure with respect to all other elements in the periodic table. Two stocks of Tb were used in the tri-arc method. One was approximately 99.67 at.% (99.97 wt.%) pure and contained the following major impurities (in ppm at.): O, 1900; C, 1100; N, 180; F, 40; Cl, 33. Another was approximately 99.89 at.% (99.99 wt.%) pure, and contained the following major impurities (in ppm at.): O, 357; C, 713; N, 23; Dy, 15; Fe, 7. The Tb used in the Bridgman method contained the following major impurities (in ppm at.): O, 1500; F, 280; C, 230; Al, 130; Fe, 130; thus it was approximately 99.77 at.% (99.97 wt.%) pure. The Si (99.9999 wt.%) and Ge (99.999 wt.%) were purchased from Meldform Metals Ltd.

The single crystal growth started with polycrystalline ingots with the same nominal chemical composition. The polycrystalline buttons were arc melted under an argon atmosphere from a mixture of appropriate quantities of constituent elements. They were turned over and re-melted several times to ensure compositional homogeneity.

For Bridgmen growth, the alloys were drop cast into a copper chill cast mold. The as-cast ingots were then electron-beam welded under vacuum into a conical tipped tungsten crucible fabricated by chemical vapor deposition. The ingots were heated in a tungsten mesh
resistance furnace under a pressure of $8.8 \times 10^{-5}$ Pa up to 1273 K (Gd$_5$Si$_2$Ge$_2$) or 1427 K (Tb$_5$Si$_2$Ge$_{1.8}$), and held at this temperature for 1 hour to degas the crucible and charge. The chamber was then backfilled to a pressure of $3.4 \times 10^4$ Pa with high-purity argon. The purpose of this over pressurization process was to equalize the pressure inside and outside of the crucible at the final temperature. The ingots were then heated to 2273 K (Gd$_5$Si$_2$Ge$_2$) or 1777 K (Tb$_5$Si$_2$Ge$_{1.8}$), and held at this temperature for 1 hour to allow thorough mixing. After this process they were withdrawn from the heat zone at a rate of 4 mm/h (Gd$_5$Si$_2$Ge$_2$) or 8 mm/h (Tb$_5$Si$_2$Ge$_{1.8}$).

For tri-arc grown crystals, arc melted buttons (weighing ~15-20 gm) were used as the charge material in a tri-arc furnace. Each of the three electrode tips were located concentrically around the outer edge of the button and positioned within 2-3 mm of the surface. A tungsten rod was used as the seed material which resulted in a randomly oriented Tb$_5$Si$_2$Ge$_{1.8}$ crystal. The crystal withdrawal rates ranged from 6 to 23 mm/hr which produced crystals roughly 3-4 mm in diameter and up to 50 mm in length.

The as-grown single crystals were oriented by back-reflection Laue x-ray diffraction. Samples with different dimensions were cut by spark erosion or electrical discharge machining. The oriented faces were prepared using standard metallographic techniques to yield flat parallel faces.

One Tb$_5$Si$_2$Ge$_{1.8}$ single crystal sample was used for the study presented in Chapters 3 and 4. It was a rectangular parallelepiped with dimensions of $1.50 \times 1.94 \times 0.88$ mm$^3$ along the $a$, $b$, and $c$-axes directions, respectively, and weighed 18.73 mg. It was from the same batch that was used in the neutron scattering study by Garlea et al. in Ref. 35, which was grown by the tri-arc method.
The Bridgman method grown $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal sample was ground into powders for the
\textit{in-situ} x-ray powder diffraction study presented in Chapter 3.

Three rectangular prismatic $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ samples were used for the study presented in Chapters 5 and 6. Their dimensions were $5.03\times0.98\times0.44 \text{ mm}^3$, $3.38\times0.94\times0.57 \text{ mm}^3$, and $4.66\times1.02\times0.82 \text{ mm}^3$. The longest dimensions were along the $a$, $b$, and $c$ axes directions, respectively. They were from two $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystals which were grown by the tri-arc method from two stocks of Tb [99.67 at.% (99.97 wt.%) and 99.89 at.% (99.99 wt.%), respectively]. The $a$- and $b$-axes samples came from the single crystal prepared using the 99.67 at.% pure Tb metal, and the $c$-axis sample came from the 99.89 at.% pure Tb.

Three $\text{Gd}_5\text{Si}_2\text{Ge}_2$ single crystal samples prepared by the Bridgman method were used for the study presented in Chapter 6. Their dimensions were $3.66\times1.82\times0.49 \text{ mm}^3$, $4.06\times1.03\times1.00 \text{ mm}^3$, and $5.6\times2.0\times0.92 \text{ mm}^3$, with the longest sides along the $a$, $b$, and $c$-axes, respectively.

One single crystal Gd sample with the dimensions of $9.12\times3.02\times1.21 \text{ mm}^3$ was used for the study presented in Chapter 6. The longest side was along the $c$-axis. It was prepared using the strain-anneal method.\textsuperscript{82} The metal was 99.89 at.% (99.98 wt.%) pure.

When the single crystal samples were subjected to measurements of dc magnetization, electrical resistance, and spontaneous generation of voltage, the misalignment between the directions of the magnetic field vector and the crystal axes was less than $\pm5^\circ$, considering the combined accuracy of crystallographic alignment and sample positioning inside the cryostat.

\subsection*{2.2. \textit{In-situ} x-ray powder diffraction}

The \textit{in-situ} x-ray powder diffraction instrument used for this thesis work was home made in the Ames Laboratory.\textsuperscript{83} It consists of three major parts, an x-ray diffractometer, a magnet,
and a cryostat. The diffractometer is standard Rigaku TTRAX system with a wide-angle goniometer and an 18 kW rotating anode x-ray source. It uses Mo Kα radiation in the Bragg-Brentano geometry. The magnet is a custom designed optical-access split-coil superconducting magnet. It provides a uniform magnetic field from 0 to 40 kOe around the sample. The cryostat is a continuous flow cryostat. The sample is cooled by flowing helium through a transfer line with a needle valve regulator. The lowest attainable temperature is 2.2 K. The temperature is stable within ±0.02 K below 50 K and within ±0.05 K above 50 K. For the in-situ x-ray powder diffraction data presented in Chapter 3, the profile residuals were between 9 and 12%, and derived Bragg residuals were between 5 and 9%. Based on the least squares standard deviations, the phase concentrations were determined with an error of less than 1%, and the interatomic distances were determined to within 0.01 to 0.03 Å.

2.3. dc magnetization measurements

Temperature and magnetic field dependencies of dc magnetization were measured in a superconducting quantum interference device (SQUID) magnetometer MPMS-XL manufactured by Quantum Design, Inc. The errors in the temperature, magnetic field, and magnetic moment were 0.5%, 1 Oe, and 1%, respectively. The SQUID is periodically calibrated to ensure that the magnetometer stays within these limits. When measuring $M(T)$, three sets of data were collected for every fixed applied magnetic field and orientation of the single crystal. The first one was collected upon heating in a constant magnetic field applied at the lowest temperature after the sample was zero-field-cooled (ZFC) from a temperature well above its Curie temperature ($T_C$). The second and third ones were collected upon cooling and heating in the same field strength as that in the first, ZFC heating measurement. The first set of data is referred to as ZFC heating, the second as field-heated (FH) cooling, and the third
one as field-cooled (FC) heating hereafter. Every isothermal $M(H)$ measurement was recorded after thermal demagnetization at 250 K and then zero field cooling down to the measurement temperature. The applied magnetic fields varied from 0 to 70 kOe with a 2 kOe step.

2.4. Electrical resistivity measurements

The electrical resistances were measured using a standard four-probe method. Four thin platinum wires were attached to the samples with H20E Epotek silver epoxy manufactured by Epoxy Technology. Typical contact resistances of the freshly prepared samples were between 1 and 2 $\Omega$. The temperature ($T$) and magnetic field ($H$) dependencies of the dc electrical resistance ($R$) were measured with a constant dc excitation electrical current ($I$) of 10 mA in the temperature range between 5 and 320 K and in magnetic fields between 0 and 40 kOe using a Lake Shore Model No. 7225 magnetometer. The external magnetic fields and excitation electrical currents were applied parallel and antiparallel to each other for all the measurements, i.e. only the longitudinal magnetostriction is considered in the present study. After loading and slowly cooling the samples, the temperature dependencies of the electrical resistance, $R(T)$, were first measured upon heating at a rate of 1 K/min from 5 to 320 K, and then upon cooling at a similar rate. Every isothermal $R(H)$ measurement was recorded after thermal demagnetization at 230 K and then slow cooling to the measurement temperature to exclude the magnetic field history dependency of the studied property.

The errors of the calculated electrical resistivity,

$$\rho = \frac{A}{l} R,$$
were about 10%, mainly due to the uncertainties in the measurement of the distance between voltage contacts, $l$, and the cross sectional area of the sample, $A$. The magnetoresistance was calculated as

$$MR = \frac{\rho(H,T) - \rho(0,T)}{\rho(0,T)}$$

where $\rho(H,T)$ and $\rho(0,T)$ represent the electrical resistivities at temperature, $T$, with and without the applied magnetic field, $H$, respectively.

2.5. Spontaneous generation of voltage measurements

The dc voltages across the samples were measured by a standard two probe method and recorded as functions of time by a Keithley 181 nanovoltmeter connected to a computer via a general purpose interface bus (GPIB) interface. Readouts from the nanovoltmeter at four times per second were computer-recorded. The temperature and magnetic field changes exerted on the samples were regulated by a LakeShore Model 7225 magnetometer. The samples were subjected to the temperature and magnetic field variations above and below their zero-field transition temperatures, at rates varying from $-7$ K/min to $+3$ K/min and from $-70$ kOe/min to $+70$ kOe/min. The magnetic fields were applied and the voltages were measured along the longest side of each sample. The misorientation between the directions of the magnetic field vector and the crystal axes were less than $\pm 5^\circ$, considering the combined accuracy of sample alignment and positioning inside the cryostat. The SGV signal backgrounds caused by a minor thermal noise and drift of the nanovoltmeter were automatically subtracted before recording every sequence. The temperature readings from the sensor may deviate from the actual sample temperature by $\pm 2$ K due to the design of the magnetometer. The resolution of the Keithley 181 nanovoltmeter is 100 nV.
2.6. Determination of $T_C$ by Arrott plots method

In order to address the coupling (or the separation) of the crystallographic and magnetic phase transitions, it is critical to determine the transition temperatures as precisely as possible. The Arrott plots\textsuperscript{84} method was used to determine the $T_C$ so as to avoid the effect of the magnetic field induced magnetization, which contrary to the spontaneous magnetization, may lead to considerable deviations\textsuperscript{85} from the material’s true $T_C$. The internal magnetic field ($H_i$) inside the sample was used to construct the Arrott plots, and it ($H_i$) was determined by subtracting the demagnetizing field from the applied field. The demagnetizing factor ($N$) was evaluated from the slope of the low-field linear regions of the $M(H)$ curves in the ferromagnetic state.\textsuperscript{86} The determined values of $N$ were consistent with the shape of the sample.
CHAPTER 3. Crystallography, Metamagnetism and MCE in Tb$_5$Si$_{2.2}$Ge$_{1.8}$

3.1. Anisotropic metamagnetism

The magnetization isotherms around $T_C$ with the magnetic field applied parallel to the $a$-axis are shown in Figure 3.1. The $T_C$ determined from the isotherms using Arrott plots (inset of Figure 3.1), is $118 \pm 1$ K. This value is in good agreement with $T_C = 120$ K reported in Ref. 35. At $T \leq 118$ K, the field dependence of the magnetization is that of a typical ferromagnet, in agreement with the microscopic magnetic structure of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ determined by neutron diffraction.$^{35}$ However, starting from $T = 119$ K (1 K above $T_C$) and at higher temperatures, the field dependence of the magnetization does not exhibit a normal paramagnetic behavior because a metamagnetic-like transition takes place. Upon increasing the magnetic field, an abrupt increase of the magnetization is observed at different, temperature-dependent critical values of the field, leading the material to technical saturation. At 119 K and 70 kOe, the magnetic moment per Tb atom reaches 7.43 $\mu_B$, which is close to the average magnetic
moment per Tb atom at 100 K – 7.58 μB – determined from the neutron scattering study of polycrystalline Tb$_5$Si$_{2.2}$Ge$_{1.8}$.$^{35}$

These field-induced magnetic transitions are reversible when $T \geq 122$ K, and they exhibit a large hysteresis (~15 kOe) between the field increasing and decreasing branches. Two features — the abrupt change in the magnetization and the hysteresis — suggest that these transitions are of first-order. The critical magnetic field (defined here as the field of the onset of the metamagnetic-like transition), $H_{cr}$, increases nearly linearly with the increasing
temperature, which is quite similar to metamagnetic-like transitions observed in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$.[87,88] However, when the magnetic field is parallel to the $b$- and $c$-axes (see Figure 3.2), a much different behavior is observed. Fields under 70 kOe do not trigger a transition along the $b$-axis, and the metamagnetic transition along the $c$-axis exhibits different features when compared to that along the $a$-axis, i.e. the transition along the $a$-axis is much sharper [compare Figure 3.1 and Figure 3.2(b)]. Furthermore, the critical fields are by ~36 kOe higher along the $c$-axis than along the $a$-axis, and the rate of change of the $H_{cr}$ with temperature for the field parallel to the $c$-axis ($5.4 \pm 0.3$ kOe/K) is much larger than the same for the field parallel to the $a$-axis ($2.64 \pm 0.02$ kOe/K). The difference in the temperature dependence of the critical fields is discussed later. The magnetization isotherms below $T_C$ [Figure 3.2(c)] show that the $a$-axis is the easy magnetization direction and the $b$-axis is the hard one. This is consistent with the microscopic magnetic structure of Tb$_5$Si$_2$Ge$_{1.8}$ in this temperature range, where a net ferromagnetic component of the magnetic moment is along the $a$-axis direction, the components along the $b$- and $c$-axes are correlated antiferromagnetically, and the moments are nearly confined in the $ac$-plane.[35]

The field-induced first-order magnetic transitions above $T_C$ (i.e. in the paramagnetic state) are generally rare. As mentioned above, similar transitions were observed in both polycrystalline[87] and single-crystal Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ along all three principal crystallographic directions,[88] and they have been regarded as magnetoelastic transformations during which the magnetic and crystal structures change concurrently.[3] According to a recent theoretical study of the electron correlation effects on the magnetostructural transition of Gd$_5$Si$_2$Ge$_2$,[29] the different polymorphs, i.e. the monoclinic and orthorhombic phases, have different $T_C$’s and, therefore, different temperature dependencies of the magnetization. Each of the two
polymorphs should order magnetically via a conventional, second order phase transition with $T^O_C$ of the orthorhombic Gd$_5$Si$_2$Ge$_2$ being considerably higher than the $T^M_C$ of the monoclinic polymorph. The actual temperature of the magnetostructural transition of Gd$_5$Si$_2$Ge$_2$, $T_C$, is located between $T^O_C$ and $T^M_C$. Hence, when a magnetic field is applied just above $T_C$, it changes the balance of the free energies between the paramagnetic monoclinic and ferromagnetic orthorhombic Gd$_5$Si$_2$Ge$_2$ phases, which in turn triggers a crystallographic transition between two polymorphs that have different magnetizations, thus leading to a discontinuous change of the magnetization at $H_{cr}$.

Given the fact that Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$ with $x \approx 0.5$ has the same sequence of polymorphs with the same types of crystal structures as Gd$_5$Si$_2$Ge$_2$, the metamagnetic-like transitions in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ are likely to have the same mechanism. Since the single ion anisotropy of Tb$^{3+}$ is considerable when compared with the negligible single ion anisotropy of Gd$^{3+}$, a different contribution may further aid in the magnetic field dependence of a structural transition in Tb$_5$Si$_{2.2}$Ge$_{1.8}$. Thus, magnetizing a material above $T_C$ should induce a small but measurable magnetostriction in a sample, resulting in a related strain that, in a way, may affect the sample similarly to an external pressure. In a polycrystalline sample, magnetic field-induced stress field should be quite complex and will be a function of the microstructure and preferred orientation, but in a single crystal it may be approximated by a uniaxial pressure.

Considering the strong dependence of the crystallographic-only transformation in Tb$_5$Si$_2$Ge$_2$ on hydrostatic pressure, the increased magnetic field, therefore, should be able to convert some or all of the high-volume monoclinic Tb$_5$Si$_{2.2}$Ge$_{1.8}$, which is an equilibrium phase above $T_C$ in a zero magnetic field, into the low-volume orthorhombic Tb$_5$Si$_{2.2}$Ge$_{1.8}$, which is stable in a zero magnetic field below $T_C$. In order to verify the sequence of crystallographic
transformations, x-ray powder diffraction measurements were carried out as a function of
temperature in constant magnetic fields of 0, 20 and 35 kOe, and as a function of magnetic
field at constant temperatures in the close proximity of $T_C$.

### 3.2. Crystallography

The intensity contour map of the x-ray powder diffraction patterns of $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$, which
were collected in a zero magnetic field during heating from 92 K to 120 K, is shown in
Figure 3.3. Remarkable differences in the positions and intensities of Bragg peaks between
the low-temperature and high-temperature patterns indicate that a structural phase transition
occurs between $\sim$102 and 112 K. The low-temperature patterns can be indexed as the
orthorhombic, space group $Pnma$, $\text{Gd}_5\text{Si}_4$-type structure [called the O(I) phase hereafter] –
major phase; and the monoclinic, space group $P112_1/a$, $\text{Gd}_5\text{Si}_2\text{Ge}_2$-type structure (henceforth,
the M phase) – minor phase. The high-temperature patterns belong to the M phase. The O(I)
to M phase transformation is accompanied by discontinuous changes of the lattice parameters
and unit cell volumes, which are $\Delta a/a = 1\%$, $\Delta b/b = 0.081\%$, $\Delta c/c = -0.16\%$, and $\Delta V/V =
0.74\%$. The structural transition proceeds via shear displacements of the adjacent layers.
along the $a$-axis in opposite directions by $\sim0.2$ Å. Along the $b$-axis, every other interlayer Si(Ge)-Si(Ge) interatomic distance expands by 22.8% – from 2.81(1) at 70 K in the O(I) phase to 3.45(3) at 110 K in the M phase – while the rest remain unchanged, including the layers themselves. These crystallographic changes are similar to those observed in Gd$_5$Si$_2$Ge$_2$ and Tb$_5$Si$_2$Ge$_2$. According to the Rietveld refinement there is a tendency towards partial ordering of Si and Ge atoms. The larger (Ge) atoms prefer (~60%) interslab positions, whereas the smaller (Si) atoms prefer (~67%) the intraslab sites, similar to the atomic distribution in Gd$_5$Si$_2$Ge$_2$.

It is worth mentioning that although the transition from the O(I) to M phase on heating is nearly complete, the inverse transition on cooling, i.e. from M to O(I), is incomplete. Even well below 100 K, 10 to 15% of the M Tb$_5$Si$_2$Ge$_2$ phase always exists. A similar phenomenon was also reported in the in-situ x-ray powder diffraction studies of Gd$_5$Ge$_4$, with ~6.5% of the high temperature phase retained at low temperatures, which was explained by existence of microstructure imperfection, such as impurities and defects.

![Figure 3.4](image.png)

Figure 3.4. The concentration of the O(I) phase as a function of temperature determined from Rietveld refinement of the patterns collected during heating and cooling of the zero-field-cooled Tb$_5$Si$_2$Ge$_2$ sample in zero (circles) and 35 kOe (triangles) magnetic fields. The arrows indicate the directions of temperature change. $T_{st}$ is the onset of the crystallographic phase transition upon cooling in a zero magnetic field. The inset illustrates the magnetization isotherms measured at selected temperatures upon field increasing from 0 to 40 kOe using the same Tb$_5$Si$_2$Ge$_2$ powder that was employed in the x-ray experiment. The magnetization was corrected for demagnetizing and replotted as $M^2$ vs. $H/M$ (Arrott plots). $T_C$ is the Curie temperature determined from the Arrott plots.
The temperature dependencies of the molar concentrations of the O(I) \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) phase derived from the Rietveld refinement of the x-ray patterns collected in zero and 35 kOe magnetic fields are shown in Figure 3.4. Upon cooling in a zero field, the M to O(I) phase transition begins at \( T_{st} = 108 \) K, which is close to the Curie temperature (110 ± 1 K) determined from Arrott plots (inset of Figure 3.4) for the same sample. The closeness of the zero-field \( T_{st} \) and \( T_C \) confirms that the extent of the decoupling of the magnetic and crystallographic phase transitions in \( \text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) alloys is composition dependent.\(^{33,35}\) We note here that the difference of the \( T_C \)'s of the powder (~110 K) and the single crystal (~118 K, Figure 3.1) samples used in this study is intrinsic, originating from a strong magnetocrystalline anisotropy (see below), as well as extrinsic, likely enhanced by small compositional differences of two different batches of samples, which has been observed in both the tri-arc and Bridgman grown cyrstals.\(^{79,80}\)

Figure 3.4 also shows that the magnetic field shifts the crystallographic phase transformation to higher temperatures and makes it less sharp, indicating that the magnetic field has a strong effect on the crystal structure change in \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) near the \( T_C \), i.e. a strong magnetoelastic effect is involved. The linear relationships between the onset temperatures of the M to O(I) crystallographic phase transitions (\( T_{st} \)'s) and the magnetic field are illustrated in Figure 3.5. The slope, \( \Delta H/\Delta T_{st} = 2.9 \pm 0.2 \) kOe/K, is nearly the same as the average value of the rate of increase of the critical magnetic field with temperature for the PM to FM metamagnetic-like transitions with the field along the \( a \)-axis (2.64 ± 0.02 kOe/K). However, along the \( b \)-axis there is no metamagnetic-like transition at fields less than 70 kOe; and for the \( c \)-axis, the value of the slope is about twice as large (5.4 ± 0.3 kOe/K). This implies a close relationship between the structural and magnetic phase transitions in \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \), which is further
supported by the results of the isothermal \emph{in-situ} x-ray powder diffraction experiments, as shown in Figure 3.6.

The magnetic field dependencies of the molar concentration of the O(I) phase determined from the x-ray powder diffraction and the bulk magnetization of the same Tb$_5$Si$_2.2$Ge$_{1.8}$ powder sample measured at the same constant temperature 112 K (2 K above $T_C$) indicate that both the crystallographic and magnetic phase transformations induced by field remain incomplete (Figure 3.6). A zero to 40 kOe magnetic field increase causes an increase of
8.8% to 36.6% of the O(I) phase content, and this trend is consistent with the change of the magnetization, which varies from ~20% to 55% of the technical saturation value assuming that the initial behavior in fields below ~10 kOe is due to domain rotation of the ferromagnetically ordered O(I), and possibly M-Tb$_5$Si$_{2.2}$Ge$_{1.8}$. The existence of a broad metamagnetic-like transition in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder is seen in the $M(H)$ behavior between ~10 and 25 kOe.

The incompleteness of this magnetic transition is evident from the magnetization of the powder at $T = 112$ K (2 K above $T_C$) and $H = 40$ kOe (only ~120 emu/g), which is far less than ~204 emu/g, value obtained in the magnetization of the single crystal Tb$_5$Si$_{2.2}$Ge$_{1.8}$ after completing a metamagnetic-like transition under similar conditions ($T = 119$ K, 1 K above $T_C$, and $H = 40$ kOe) with the field parallel to the $a$-axis. The incompleteness of the magnetic phase transition in the powder is likely associated with the magnetocrystalline anisotropy of Tb$_5$Si$_{2.2}$Ge$_{1.8}$. A 40 kOe magnetic field can only induce the metamagnetic-like transitions in the grains with their $a$-axis directions parallel or nearly parallel to the applied field. Assuming complete randomness in the powder sample, about 1/3 of the grains will be close to fulfilling this constraint and undergo the transition, which matches the observed changes in the crystallography and magnetism fairly well. This correlation of the degrees of incompleteness of crystallographic and magnetic phase transitions once again indicates an intimate relationship between the crystalline and magnetic sublattices, supporting the notion that the metamagnetic-like transition in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is a coupled magnetostructural transition, similar to that observed in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$. Although the magnetocrystalline anisotropy results in some complications, such as making the field-induced structural transition in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ dependent on the direction of the field, the atomic scale mechanism, i.e. the
field-induced displacements of the atomic layers along the \(a\)-axis, remains identical for both the \(\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}\) and \(\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4\) systems.

### 3.3. Anisotropic magnetocaloric effect

Since the crystal structure change brings an additional contribution from the lattice during the transition, the magnetocaloric effect of a material exhibiting a magnetostructural transition is usually much stronger than that of a conventional ferromagnet with only a magnetic contribution.\(^{24}\) Thus, it is reasonable to expect greater values of the magnetocaloric effect when magnetic field is applied parallel to the \(a\)- and \(c\)-axes than when the field is parallel to the \(b\)-axis in \(\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}\). The magnetocaloric effect, \(-\Delta S_M\), was evaluated from the \(M(H)\) data according to the Maxwell relation \((\partial S_M/\partial H)_T = (\partial M/\partial T)_H\), and the results are displayed in Figure 3.7. As expected, the maximum values of the \(|\Delta S_M|\) with field along the \(a\)- and \(c\)-axes (40 ± 2 and 38 ± 2 J/kg K, respectively, for \(\Delta H = 50\) kOe) are much greater than the values obtained with field parallel to the \(b\)-axis (3.6 ± 0.2 J/kg K) or the bulk polycrystalline \(\text{Tb}_5\text{Si}_2\text{Ge}_2\) (13.4 J/kg K) reported by Morellon \textit{et al}.\(^{34}\), which is about a half of the value obtained in this research (see below), under the same conditions. Since the temperature
dependencies of the critical fields are different for the field parallel to the $a$- and the $c$-axes (Figure 3.1, Figure 3.2, and Figure 3.5), accordingly, the $-\Delta S_M(T)$ curves are also quite different.

The magnetocaloric effect of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder is $26 \pm 1$ J/kgK for $\Delta H = 50$ kOe, which is close to the average value, 27 J/kgK, over the three main crystallographic directions of the single crystal under the same conditions. The $|\Delta S_M|$ of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder is also much smaller than that of its counterpart in the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ family, Gd$_5$Si$_{1.0}$Ge$_{2.9}$, whose $|\Delta S_M|$ is 62 J/kgK for $\Delta H = 50$ kOe at $T_C = 140$ K. This is understandable because the magnetocrystalline anisotropy of the Gd-containing compound is much smaller than that of the Tb-containing material.

Additional reduction of the magnetocaloric effect in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound compared to Gd$_5$Si$_{1.0}$Ge$_{2.9}$ is related to the differences in the completeness of the structural transitions and in the non-negligible crystalline electric field effects present in the Tb-containing compound. The $|\Delta S_M|$ of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder is about twice that of the bulk polycrystalline Tb$_5$Si$_2$Ge$_2$ (13.4 J/KgK for $\Delta H = 50$ kOe). Given that the magnetic and structural transitions in Tb$_5$Si$_2$Ge$_2$ are decoupled, the enhancement of the magnetocaloric effect in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder may be explained by the magnetic-field-induced crystallographic phase transition overlapping with the ferromagnetic ordering. This conclusion finds further support in the fact that when both transitions in Tb$_5$Si$_2$Ge$_2$ are recoupled by hydrostatic pressure, $|\Delta S_M|$ here reaches ~22.1 J/kgK, which is close to that observed in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ at atmospheric pressure.

Overall, the magnetocaloric effect of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ exhibits an extremely strong anisotropy (Figure 3.7), which directly correlates with the differences in the magnetic hardness along the
three principal crystallographic directions – the easier it is to fully magnetize the material, the stronger is the magnetocaloric effect. As far as we are aware, such an extreme anisotropy of the magnetocaloric effect has not been observed among the members of the $R_5(Si_xGe_{1-x})_4$ family nor among other materials for which the anisotropy of the magnetocaloric effect has been studied.\textsuperscript{89-91}

![Figure 3.8. Temperature dependencies of the inverse magnetic susceptibility, $H/M$, of $Tb_5Si_{2.2}Ge_{1.8}$ measured on heating in a 50 kOe magnetic field parallel to the $a$-, $b$-, and $c$-axes. The lines are linear least squares fits of the data to the Curie-Weiss law between 200 and 300 K. The inset table gives the paramagnetic Curie temperatures ($\theta_p$’s) and effective magnetic moments ($\mu_{\text{eff}}$’s) derived from these linear least squares fits, where the numbers in parenthesis represent the uncertainties in the last significant digits determined from the corresponding least squares standard deviations.](image)

The anisotropic behavior of the metamagnetic-like transition and magnetocaloric effect in $Tb_5Si_{2.2}Ge_{1.8}$ can be understood from the magnetocrystalline anisotropy originating from crystalline electric field interactions, as has been reported in other rare-earth intermetallic compounds with distinctly anisotropic crystal lattices and non-spherical $4f$ electron wave functions of the lanthanide.\textsuperscript{92-96} The persistence of the magnetocrystalline anisotropy in the paramagnetic state of $Tb_5Si_{2.2}Ge_{1.8}$ is seen in the temperature dependencies of the inverse magnetic susceptibility along three main crystallographic directions in Figure 3.8. The paramagnetic Weiss temperatures ($\theta_p$’s) were derived from a least squares fit of the experimental data to the Curie-Weiss law over the temperature range of 200 to 300 K for the magnetic field parallel to the $a$-, $b$-, and $c$-axes. The respective $\theta_p$’s are 117.3(1), 80.93(4), and 105.8(1) K, and the corresponding effective magnetic moments ($\mu_{\text{eff}}$’s) are 10.152(2),
10.047(1), and 10.091(1) $\mu_B$ per Tb atom, where the numbers in parenthesis represent the uncertainties in the last significant digits determined from the corresponding least squares standard deviations. The moments are slightly larger than the theoretical value $g\sqrt{J(J+1)} = 9.72 \mu_B$, which is probably due to non-negligible contribution from 5$d$ conduction electrons, observed in many $RM_x$ compounds and the pure metals themselves.

Among the three principal crystallographic directions, the values of the $\theta_p$’s and $p_{eff}$’s for the magnetic field along the $a$-axis are the greatest, and those for the $b$-axis are the smallest, indicating that the $a$-axis remains the magnetic easy axis and the $b$-axis is the hard direction in the paramagnetic state. Since the alignment of the magnetic moments with the field induces a strain that should be proportional to the magnetization in the paramagnetic state, the resultant stress under the same magnitude of the magnetic field along the $a$-axis would be greater than that for the $c$- and $b$-axes, thus explaining the lower critical magnetic fields along the $a$-axis. A sufficient field-induced stress, in turn, induces the monoclinic to orthorhombic crystallographic transition above the zero magnetic field $T_C$. Similar to Gd$_5$Si$_2$Ge$_2$, the two Tb$_5$Si$_{2.2}$Ge$_{1.8}$ phases are expected to have different temperature dependencies of the magnetization, and the observed anisotropic magnetization behavior (Figure 3.1 and Figure 3.2) resembles anisotropic metamagnetic-like transformations.

The coupling of the magnetic and crystallographic phase transitions by applying a magnetic field at temperatures greater than $T_C$ in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ echoes the similar coupling induced by a hydrostatic pressure in Tb$_5$Si$_2$Ge$_2$. This behavior is different from that observed in Gd$_5$(Si$_x$Ge$_{1-x})_4$, where the crystallographic and magnetic phase transitions between the two polymorphs remain coupled for any magnetic field less than 100 kOe, or any pressure between 1 bar and 9 kbar over a composition range of $0 \leq x \leq 0.5$. For Tb$_5$Si$_2$Ge$_2$ under
ambient pressure, the decoupling of the magnetic and structural transitions is $\sim$10 K,\textsuperscript{33} which is larger than 5 K or less observed in Tb$_5$Si$_{2.2}$Ge$_{1.8}$. Furthermore, magnetic fields under 120 kOe could not induce the metamagnetic-like transition in Tb$_5$Si$_2$Ge$_2$ above $T_C$.\textsuperscript{33} Thus, unlike Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, the coupling/uncoupling of the magnetic and structural transformations is composition, magnetic field, and pressure dependent in Tb$_5$(Si$_x$Ge$_{1-x}$)$_4$. This difference in the behaviors of these two closely related systems should be attributed to the single ion anisotropy of Tb, which in addition to indirect exchange interactions that are dominant in both systems, introduces a non-negligible magnetoelastic component in the Tb-based materials.
CHAPTER 4. Magnetic Phase Transitions and Ferromagnetic Short-Range Correlations in Single Crystal Tb₅Si₂.2Ge₁.₈

4.1. Temperature dependencies of the magnetization in 10 and 50 kOe applied field

Temperature dependencies of the magnetization of single crystal Tb₅Si₂.2Ge₁.₈ measured in a 10 kOe magnetic field applied along the $a$, $b$, and $c$-axes directions between 1.8 and 200 K are shown in Figure 4.1. The FC heating and FH cooling data overlap over the entire temperature range except for small differences at $T_C$, i.e. hystereses along the $a$ and $c$-axes, and a spike along the $b$-axis. Thus, only ZFC heating and FH cooling data are displayed for clarity.

The $M(T)$ behaviors shown in Figure 4.1 exhibit several noteworthy features. First, below $T_C \approx 120$ K, the magnitudes of the magnetization with $H\parallel a$ and $H\parallel c$ are much greater than those with $H\parallel b$. This is in line with the magnetic structure of this compound, where the magnetic moments are mainly confined to the $ac$ plane (see Figure 1.4). Second, a cusp in the $H\parallel a$ and $H\parallel b$ $M(T)$ curves, and a minimum in the first derivative of magnetization with respect to...
temperature \( (dM/dT) \) with \( H \parallel e \) (inset of Figure 4.2) are consistent with a spin reorientation transition at \(~70\ K\). With \( H \parallel a \), the magnetization increasing on heating from 2 to 70 K is in agreement with decreasing of the average angle that the Tb moments form with the \( a \)-axis from 38.4° at 4.2 K to 9.3° at 75 K.\(^{35}\) From 70 to about 120 K magnetization with \( H \parallel a \) shows a typical ferromagnetic behavior as the magnetic structure along the \( a \)-axis remains unchanged. The magnetic moment component along the \( c \)-axis switches from a ferromagnetic to an antiferromagnetic configuration upon heating through 70 K.\(^{35}\) This corresponds to a change of the sign of \( dM/dT \) when the magnetic field is parallel to the spin axis, \( i.e.\) the ferromagnetic susceptibility decreases, while an antiferromagnetic susceptibility increases upon heating. Consequently, a \( dM/dT \) minimum is formed at 70 K with \( H \parallel e \).

When \( H \parallel b \), the magnetization values initially decrease with increasing temperature from 1.8 K, form a minimum at about 40 K, and then reach a maximum at 70 K. Contrary to \( H \parallel a \) and \( H \parallel c \), this behavior does not follow the thermal evolution of the \( b \)-axis components of spontaneous magnetic moments in zero field.\(^{35}\) Recalling that measured magnetization also manifests the ability of the external field to overcome the magnetocrystalline anisotropy energy, magnetostatic energy, and thermal fluctuations to align the moments in the field direction, the complicated thermal variation of the magnetization with \( H \parallel b \) may reflect the thermal dependence of the magnetic anisotropy energy. When \( 70 \ K < T < \sim120 \ K \), the magnetization with \( H \parallel b \) continuously decreases upon heating. Upon FH cooling, however, a sharp spike develops at 118 K. The explanation of the physical origin of this singularity will be given below during the \( \text{Tb}_3\text{Si}_{2.2}\text{Ge}_{1.8} \), see Section 4.3.

The magnetic order-disorder transition, which occurs around 120 K, shows a thermal hysteresis of 4 K when \( H \parallel a \) and \( H \parallel c \), which signifies a first-order phase transition, but the
hysteretic behavior is different when $\mathbf{H} \parallel \mathbf{b}$. In the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ family with $\text{R} = \text{Gd}$, the first-order magnetic order-disorder transition is always a coupled magnetic and crystallographic phase transition.\textsuperscript{19} For example, in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound, which is analogous to $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$, the transformation from a high temperature monoclinic to a low temperature orthorhombic phase is simultaneously accompanied by a paramagnetic to ferromagnetic transition. In $\text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4$, however, these two transitions (magnetic and crystallographic) may be decoupled, and the extent of decoupling is composition dependent.\textsuperscript{33-35} Since decoupling in $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ is less than 5 K, and the two transitions can be recoupled by applying $\mathbf{H} \geq 10$ kOe when $\mathbf{H} \parallel \mathbf{a}$ (see Chapter 3), the magnetic order-disorder transitions shown in Figure 4.1 with $\mathbf{H} \parallel \mathbf{a}$ and $\mathbf{H} \parallel \mathbf{c}$ are likely coupled magnetostructural phase transformations. The difference in hysteretic behavior when $\mathbf{H} \parallel \mathbf{b}$ is due to the fact that the 10 kOe magnetic field is not strong enough to align the moments in the field direction. This explanation is consistent with temperature dependencies of the magnetization measured in a 50 kOe applied magnetic field, which are shown in Figure 4.2. Only ZFC heating and FH cooling results are displayed here because the ZFC and FC heating data are identical.

![Figure 4.2. Temperature dependencies of the magnetization of $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ measured in a 50 kOe magnetic field applied parallel to the $a$-, $b$-, and $c$-axes upon ZFC heating (open symbols) and FH cooling (solid symbols). Note that the temperature scale is the same for all three orientations.](image_url)
From Figure 4.2, one can see that the magnetic order-disorder transitions exhibit very similar thermal hystereses regardless of the direction of the 50 kOe magnetic field. The magnitudes of the magnetization at temperatures immediately below the ferromagnetic to paramagnetic transition are equivalent to 6.7, 3.1, and 5.1 $\mu_B$ per Tb atom with $H||a$, $H||b$, and $H||c$, respectively. Taking the value with $H||a$ as a reference, the relative collinearity of the magnetic moments with applied magnetic field is 100, 47, and 76% with $H||a$, $H||b$, and $H||c$, respectively. Similarity of hysteretic behaviors shown in Figure 4.2 with those observed in numerous Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ compounds indicates that when a sufficient fraction of magnetic moments is aligned with the external field, the magnetic order-disorder transition in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ becomes first-order and is likely a coupled magnetic and crystallographic phase transition. The transition takes place at different temperatures when the 50 kOe magnetic field is applied along different directions. Consistent with the relative collinearity of the moments, the transition temperature is the highest with $H||a$, the lowest with $H||b$, and it is intermediate with $H||c$. This is expected because states with greater disorder ($H||b$ and $H||c$) can be destroyed by lower thermal energy. Moreover, wider hystereses are associated with lower magnetic ordering temperatures when $H||b$ (~6 K) and $H||c$ (~5 K) compared to ~4 K when $H||a$. The hysteresis generally arises from the need to overcome some energy barriers separating neighboring low energy states, which in this case, is mainly strain due to the crystallographic phase transformation. As the transition temperature lowers, the widening hysteresis reflects complexity of the energy landscape in Tb$_5$Si$_{2.2}$Ge$_{1.8}$.

Figure 4.2 also shows that the spin reorientation transition either shifts to lower temperature in a 50 kOe magnetic field ($H||b$) or becomes indistinguishable ($H||a$ and $H||c$) when compared to the 10 kOe data of Figure 4.1. This is expected because at $T_{SR}$, the orientations of Tb moments change within the $ac$ plane, and applying higher magnetic field within the
same plane is more effective in aligning the moments. Consequently, $T_{SR}$ becomes indistinguishable when the moments remain mostly aligned with the 50 kOe field regardless of temperature as long as it remains below $T_C$.

The significant difference between the temperature dependence of the magnetization with 10 and 50 kOe external fields applied parallel to the three principal crystallographic axes indicates a complicated thermal evolution of the magnetic structure of Tb$_5$Si$_2$Ge$_{1.8}$ in the presence of external magnetic fields. This may be further probed by measuring magnetization isotherms at different temperatures with magnetic field applied along the three major crystal axes.

4.2. Magnetization isotherms between 1.8 and 70 K

Figure 4.3 shows the magnetization isotherms of the Tb$_5$Si$_2$Ge$_{1.8}$ single crystal measured at 1.8 K. The magnetization with $H||a$ involves a two-step process. The first step corresponds to the domain wall movement when the applied field is increased from 0 to 6 kOe and it then continues as a slow increase of the magnetization due to a coherent rotation of magnetic moments towards the direction of the applied field from 8 to 38 kOe. Two facts are noted: (i)
no hysteresis occurs when the applied field is greater than 10 kOe, and (ii) the magnetization at $H = 10$ kOe is $7.4 \, \mu_B$ per Tb atom, which is close to the value of the average $a$-axis component ($7.3 \, \mu_B$ per Tb atom) obtained from the neutron diffraction study. Hence, from 10 to 38 kOe, the material is a single domain with a major ferromagnetic component of all magnetic moments along the $a$-axis (see Figure 1.4). Note, that at this point the magnetic moments in the domain have substantial canting angles with the $a$-axis. The second step of magnetization starts with a rapid increase when the applied field is between 40 and 48 kOe, indicating that the magnetic structure of $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ has changed. This step brings a nearly full alignment of moments along the external field direction because the magnetization value at $H = 48$ kOe is $9.3 \, \mu_B$ per Tb atom, close to the $9.4 \, \mu_B$ per Tb atom obtained from the neutron diffraction measurements at 4.2 K, and to the theoretically expected value of $gJ = 9 \, \mu_B$. The excess of $0.3 \, \mu_B$ reflects contribution from itinerant 5d electrons of Tb. There is only a narrow hysteresis associated with this magnetic phase transition.

Since the magnetic moments are mainly confined to the $ac$ plane of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ crystal lattice, the nearly linear increase of the magnetization upon increasing the applied field from 0 to 46 kOe in the $b$-axis direction is due to a continuous rotation of the magnetic moments towards the external field direction. This rotation is reversible, and consequently, there is no hysteresis. A discontinuous increase by $1.9 \, \mu_B$ per Tb atom occurs between 46 and 50 kOe. This discontinuity indicates a sudden change of the orientation of some of the magnetic moments when the external field overcomes the anisotropy energy. This field-induced magnetic phase transition may be a result of flipping the moments at the Tb1 sites (see Figure 1.4) out of the $ac$ plane and becoming parallel to the $b$-axis. Recall that the Tb1 moments are perpendicular to the $b$-axis in a zero magnetic field. Of the Tb sites in the $\text{Sm}_5\text{Ge}_4$-type
structure, 20% are Tb1 sites and the remaining 80% are equally divided between Tb2 and Tb3. Thus, flipping all Tb1 moments from perpendicular to parallel to the external field, should suddenly increase magnetization by ~20% of the full magnetic moment of the Tb atom ($9.3 \mu_B \times 20% = 1.9 \mu_B$). A hysteresis of about 2 kOe accompanies this transition, which also indicates a strong magnetoelastic effect.

Although the magnetic moments are mainly confined to the $ac$ plane, the magnetization at 1.8 K with $H||c$ shows quite different features from that with $H||a$. First, there is a hysteresis between the field increasing and decreasing branches over the entire range of fields, suggesting that besides being dominant during the initial magnetization process between 0 and 6 kOe, the domain wall movements accompany the coherent magnetic moment rotation between 8 and 70 kOe. Second, the magnitude of the magnetization at $H = 10$ kOe, equivalent to $5.2 \mu_B/Tb^{3+}$, is only slightly smaller than $5.5 \mu_B$ -- the $c$-axis component of the spontaneous magnetization at 4.2 K. These two observations mean that the material is close to but not completely in a single domain state when the applied field is greater than 10 kOe and applied in the $c$-axis direction. Therefore, domain walls are not as mobile when $H||c$ when compared to $H||a$. Consequently, a smaller remanent magnetization mainly due to domain wall pinning is observed with $H||c$ than with $H||a$. Third, the absence of magnetization jump(s), such as those observed with $H||a$ between 40 and 48 kOe, and with $H||b$ between 46 and 50 kOe, indicates that there is no field-induced magnetic phase transition below 70 kOe with $H||c$. This is in line with the neutron diffraction observation$^{35}$ that the Tb moment projection along the $c$-axis is ferromagnetic at low temperature.

The magnetic phase transitions that occur at 1.8 K when the magnetic field is applied along the $a$- and $b$-axes directions result from a competition between the magnetocrystalline
anisotropy and the external field. Since the magnetocrystalline anisotropy generally varies with temperature, it is reasonable to expect such transitions to occur at different critical magnetic fields as temperature varies. When the system reaches the spin reorientation temperature, $T_{SR} = 70$ K, the magnetic moments are almost collinear in the $a$-axis direction, therefore, the magnetic field applied in this direction needed to induce the magnetic phase transition isothermally should be lower. This is indeed the case when the magnetization of the $\text{ Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal was measured isothermally as a function of applied magnetic field between 1.8 and 70 K; representative isotherms at 10, 40, and 70 K are shown in Figure 4.4.

![Magnetization isotherms](image)

**Figure 4.4.** Magnetization isotherms of $\text{ Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ measured with the applied magnetic field parallel to the $a$-, $b$-, and $c$-axes and varying from 0 to 70 kOe at 10, 40, and 70 K. The open symbols are field increasing and the solid symbols are field decreasing data points.

The values of the critical fields decrease with increasing temperature, indicating a reduction of the magnetocrystalline anisotropy energy. The magnetization steps during the field-
induced transitions also decrease with increasing temperature from ~0.8 \( \mu_B \) at 10 K to ~0.3 \( \mu_B \) at 40 K to zero at 70 K, reasonably closely following the decrease of tilting angles of magnetic moments with the \( a \)-axis. The field-induced transition along the \( b \)-axis also disappears at \( T_{SR} = 70 \) K. The magnetization at 70 kOe and 70 K is 4.3 \( \mu_B \), which is close to that at 70 kOe and 40 K (4.9 \( \mu_B \)). Therefore, the absence of a sharp field-induced transition along the \( b \)-axis at and above 70 K indicates that the Tb moments are coherently rotated from the \( ac \)-plane to the \( b \)-axis upon the increasing of the external magnetic field.

The magnetization isotherms with the applied field along the \( c \)-axis direction show a departure from the ferromagnetic behavior with increasing temperature, which is consistent with the tilting of the magnetic moments away from this direction when temperature increases from 1.8 to 70 K. No field-induced magnetic phase transition with \( H || c \) is observed in Figure 4.4. Therefore, between 1.8 and 70 K, the field-induced magnetic phase transitions occur with \( H || a \) and \( H || b \), but not with \( H || c \) when the magnetic field is less than 70 kOe. On the contrary, when temperatures are in the vicinity of or above the \( T_C \) of Tb\(_5\)Si\(_2\)Ge\(_{1.8}\), field-induced magnetic phase transitions occur when the external field is along the \( a \)- and \( c \)-axes directions but not the \( b \)-axis (See Figure 3.1 and Figure 3.2). This difference suggests a strong thermal variation of the magnetic anisotropy energy.

### 4.3. Anisotropic ferromagnetic short-range correlations

Figure 4.5 illustrates the temperature dependencies of the inverse dc magnetic susceptibilities \((H/M)\) of Tb\(_5\)Si\(_2\)Ge\(_{1.8}\) measured during FC heating from 1.8 to 300 K with a 10 Oe magnetic field applied along the \( a \), \( b \), and \( c \)-axes. The Griffiths phase-like behavior is evident by a characteristic negative deviation\(^{66}\) from the Curie-Weiss behavior and less-than-unity
magnetic susceptibility exponents between $T_C$ (118±2 K) and $T_G$. The latter is the critical Griffiths temperature of 200±2 K as marked in Fig. 4.6, taken as the temperature where the $H/M$ curves start deviating from the Curie-Weiss behavior.

The inset of Figure 4.5 shows the logarithmic representation of the main panel data ($H/M$ vs. $T$) and their fitting to the relation $\chi^{-1} \propto (T-T_C^{rand})^{1-\lambda}$, where $T_C^{rand}$ is an adjustable parameter, and $\lambda$ is the magnetic susceptibility exponent parameter. In the conventional paramagnetic phase above $T_G$, $\lambda_{PM}$ is zero and isotropic. In the Griffiths phase regime between $T_C^{rand}$ and $T_G$, both the negative deviations and $\lambda_G$ are anisotropic. The most pronounced negative deviation and the largest $\lambda_G$ are found when the magnetic field is parallel to the $a$-axis, which is the magnetic easy axis at temperatures below $T_C$. This observation is in line with the report that in single crystal Gd$_x$Ge$_y$ the magnetic susceptibility along its easy magnetization direction always exhibits a greater deviation from Curie-Weiss behavior when compared to the other two major crystallographic directions below its $T_G$. The observed anisotropy is reasonable considering that the Griffiths-like phase originates from a system of ferromagnetic
clusters in the paramagnetic phases of both single crystal Gd₅Ge₄\textsuperscript{76} and polycrystalline Tb₅Si₂Ge\textsubscript{2}\textsuperscript{75}.

It is interesting to note that the differences in Weiss temperatures are consistent with the anisotropy of the layered crystal structure (see Figure 1.4) of the compound and are consistent with the current understanding of the nature of magnetic exchange interactions in the family of \(R_5T_4\) compounds, where \(T\) is Si or Ge. It is known that the \(–R–T–T–R–\) network plays a significant role in defining magnetic interactions.\textsuperscript{29,97} Within each slab, the network of strongly interacting \(–Tb1–T1–T2–Tb1–\) atoms is two dimensional and it remains intact in both the paramagnetic and magnetically ordered states. The three-dimensionality of the network is restored only in the magnetically ordered state when the monoclinic phase transforms into the orthorhombic Tb\(_5\)Si\(_{2.2}\)Ge\(_{1.8}\) in which the \(–Tb1–T3–T3–Tb1–\) network also exists (it is absent on the monoclinic phase where T3-T3 bonds are too long). Hence, strong pseudo-two dimensional interactions in the planes of the slabs (\(ac\) plane) are reflected in the higher Weiss temperatures for \(H∥a\) and \(H∥c\).

The anisotropy of the ferromagnetic clusters in the Griffiths phase-like state of Tb\(_5\)Si\(_{2.2}\)Ge\(_{1.8}\) is also evident from the thermal history dependence of the dc magnetization measured in a 10 Oe applied magnetic field when \(T_C < T < 150\) K, Figure 4.6. Here, the magnitude of magnetization is substantially greater when \(T_C\) is approached upon cooling than upon heating. This difference is greater the closer the system is to \(T_C\). The resulting inverse thermal hysteresis, which is in contrast to a conventional thermal hysteresis where the magnetization measured at the same temperature upon heating is greater than that upon cooling (Figure 4.2), occurs because the magnetic and crystallographic phase transitions in the Tb\(_5\)Si\(_{2.2}\)Ge\(_{1.8}\) compound are decoupled by less than 5 K in zero and weak applied magnetic fields.
Thus, the magnetic ordering on cooling starts with the ferromagnetic ordering of the monoclinic phase. This second-order, purely magnetic phase transition, is preceded by growth of both the size and number of the monoclinic ferromagnetic clusters, which is responsible for the rapid increase of the magnetization when the temperature approaches 117 K from $T > T_C$ (Figure 4.6). The drastic decrease of the magnetization from 117 to 115 K when $H \parallel a$ and $H \parallel b$ may be understood if one assumes that the crystallographic phase transition from the monoclinic to orthorhombic phase occurs over this temperature.

It has been established both theoretically and experimentally that in the closely related $R_5T_4$ compounds with $R = $ Gd, the Curie temperature of the orthorhombic $Gd_5Si_4$-type polymorph is much higher than that of the monoclinic $Gd_5Si_2Ge_2$-type phase. By analogy, and also considering preliminary theoretical modeling results, the orthorhombic $Tb_5Si_{2.2}Ge_{1.8}$ has a higher $T_C$ when compared to the monoclinic $Tb_5Si_{2.2}Ge_{1.8}$. Thus, on cooling to 115 K much of the monoclinic ferromagnetic $Tb_5Si_{2.2}Ge_{1.8}$ single crystal
transforms to the orthorhombic ferromagnetic structure, and $T_C$ of the latter is considerably greater than 115 K.

Given that anisotropy constants generally increase when temperature is below $T_C$, and considering a strong single ion anisotropy of the Tb$^{3+}$ ion, the anisotropy energy of the orthorhombic ferromagnetic Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is expected to be much greater than that of the monoclinic ferromagnetic Tb$_5$Si$_{2.2}$Ge$_{1.8}$ at 115 K. Obviously, the orthorhombic magnetic domains form concurrently with the crystallographic phase transformation. Yet, a 10 Oe field is not large enough to move the domain walls of the orthorhombic ferromagnetic Tb$_5$Si$_{2.2}$Ge$_{1.8}$ at 115 K. This leads to an abrupt decrease of the magnetization values upon cooling through the crystallographic phase transition temperature. On heating, the structural transition is shifted by 4 to 5 K towards higher temperature, (see Chapter 3) but the $T_C$ of the monoclinic phase remains the same, and overall, the transition is between the orthorhombic ferromagnetic and the monoclinic paramagnetic polymorphs of Tb$_5$Si$_{2.2}$Ge$_{1.8}$. As a result, the magnetization values measured on heating are lower than those during cooling. This model of the anomalous thermal hysteresis in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ when $T_C < T < 150$ K is supported by the following observations. First, the inverse hysteresis disappears along the $a$- and $c$-axes when the field is increased to 1000 Oe, as shown in Figure 4.7, indicating that coercive fields along these two directions are lower than 1000 Oe. Second, the thermal history dependencies of the magnetization in a 100 Oe magnetic field (see Figure 4.8) applied along the $a$- and $c$-axes show a crossover behavior between the 10 and 1000 Oe field data. Finally, the thermal irreversibility near $T_C$ remains unconventional and abnormal along the $b$-axis even in fields as high as 10 kOe (see Figure 4.1 and Figure 4.6 to Figure 4.8). In other words, while the thermal irreversibility anomalies may be
suppressed by the external magnetic field, it is most difficult to do so with the field along the $b$-axis. This is consistent with the $b$-axis being the magnetically hard axis, and the $a$-axis (and the $c$-axis) being the easy axes of the orthorhombic Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound as seen in Figure 4.3 and Figure 4.4. It is well-known that when a magnetic field is applied parallel to the easy axis in a demagnetized system, domain wall displacements dominate the magnetization process, which is on the other hand dominated by spin rotations when the applied field is parallel to the hard axis of a system with a strong intrinsic anisotropy. Consequently, domain walls are easier to move when the magnetic field is applied along the $a$- and $c$- than the $b$-axis of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal, leading to a much more persistent hysteresis anomaly along the $b$-axis.

The larger magnitude of magnetization upon FH cooling when compared to FC heating in small magnetic fields (but not the sharp drop during cooling as in Tb$_5$Si$_{2.2}$Ge$_{1.8}$) has also been observed in a Gd$_3$Ge$_4$ single crystal. It was ascribed to short-range ferromagnetic correlations in both the paramagnetic and antiferromagnetic phases of the compound. These short-range...
ferromagnetic correlations originate from a competition between the interslab and intraslab magnetic exchange interactions. In the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound, the anomalous hysteresis away from $T_C$ is of a similar origin as the one in the Gd$_5$Ge$_4$ compound, but it is the decoupling of the magnetic and crystallographic phase transitions that defines the anomalous behavior of the magnetization in the immediate vicinity of $T_C$.

Conventional hysteresis occurring at $T_C$ when the 1000 Oe magnetic field is applied along the $a$- and $c$-axes has two factors in its origin. First, with increasing external field, the contribution from ferromagnetic clusters (Griffiths phase) becomes less visible (is quenched) due to an increased contribution from the paramagnetic matrix. Second, at $T < T_C$, the net magnetization increases because the external field exceeding the coercive field increases the volume of the domains with spins oriented in the direction favored by the external field. At $T_C$, the magnetization from ferromagnetic monoclinic Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is no longer greater than that from the oriented magnetic domains of the orthorhombic magnetic phase transition sets in. Obviously, this critical field should be markedly different along different crystallographic
directions due to strong magnetocrystalline anisotropy below $T_C$. The persistence of the inverse hysteresis at 10 kOe applied along the magnetic hard $b$-axis is the manifestation of this mechanism.

4.4. Magnetic phase diagram

Based upon the magnetization data from the present and previous chapters, the magnetic phase diagrams of Tb$_5$Si$_2.2$Ge$_1.8$ with the magnetic field applied along the three major crystallographic directions are constructed and displayed in Figure 4.9. It is worth mentioning that the $M(H)$ and $M(T)$ data are in excellent agreement with one another.

The magnetically ordered phases are denoted as FM for the canted ferromagnetic structure observed in a zero magnetic field between $T_{SR}$ and $T_C$, and SR-FM for a
different canted ferromagnetic structure, which is observed in a zero field below $T_{SR}$. The phase boundaries separating SR-FM and FM states with $H\parallel a$ and $H\parallel b$ closely follow one another, but they do not coincide. A similar phase boundary when $H\parallel c$ cannot be traced using $M(H)$ behavior because no obvious field-induced phase transition is observed here. These phase diagrams show a strong anisotropic behavior of the magnetic order-disorder transitions. Phase boundaries between the paramagnetic (PM) and magnetically ordered states for the three directions are considerably different from each other. For instance, magnetic field applied along the $a$-axis has a strong effect on $T_C$ ($dT_C/dH$ approaches 0.4 K/kOe). On the other hand, when the field is applied along the $b$- and $c$-axes, $dT_C/dH$ is lower by a factor of 4 to 5.
CHAPTER 5. Electrical Resistivity and Magnetoresistance of Single Crystal $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$

5.1. Temperature dependencies of the electrical resistivity along the $a$-axis

The temperature dependencies of the electrical resistivity upon heating and cooling between 5 and 320 K in zero and 20 kOe magnetic fields applied along the $a$-axis of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal are shown in Figure 5.1. The value of the electrical resistivity at 5 K in a zero magnetic field (the first data point of the measurements) is about 300 $\mu$Ω cm and is of the same order of those observed in $\text{Tb}_5\text{Si}_2\text{Ge}_2$ and $\text{Tb}_5\text{Si}_{2.4}\text{Ge}_{1.6}$ polycrystalline samples.\textsuperscript{33,40} A local maximum is observed in the first derivative of the electrical resistivity with respect to temperature, $d\rho/dT$, at about 70 K, as shown in the inset of Figure 5.1, corresponding to the spin reorientation transition as shown in Ref. 35 and Chapter 4. This anomaly has no thermal or magnetic field hysteresis, and therefore, only one curve measured upon heating in a zero magnetic field is shown for clarity. The most distinct features in Figure 5.1 are the discontinuous changes of the electrical resistivity observed between 110 and 129±1 K, which depends on the direction of the temperature variation, i.e. heating or cooling, and the value of
the applied magnetic field. An 8±1 K thermal hysteresis between heating and cooling affecting the discontinuities is seen both with and without the applied magnetic field. The origin of this feature is a first-order phase transformation between the low temperature orthorhombic and high temperature monoclinic structures; the latter in agreement with previous studies of this compound using the neutron powder and single crystal diffraction,\textsuperscript{35} \textit{in-situ} x-ray powder diffraction, and magnetization techniques described in Chapter 3.

It is interesting to note that the electrical resistivity of the Tb\textsubscript{5}Si\textsubscript{2.2}Ge\textsubscript{1.8} single crystal along the \textit{a}-axis is high at low temperatures, contrary to low resistance states at low temperatures observed in polycrystalline Gd\textsubscript{5}Si\textsubscript{1.0}Ge\textsubscript{3.6}, Gd\textsubscript{5}Si\textsubscript{1.1}Ge\textsubscript{2.2}, Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{2}, and Tb\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{2},\textsuperscript{10,32,33,39,78,99} however, it is similar to high resistance low temperature states of the polycrystalline Gd\textsubscript{5}Si\textsubscript{1.5}Ge\textsubscript{2.5}, Gd\textsubscript{5}Si\textsubscript{1.9}Ge\textsubscript{2.05}, and Tb\textsubscript{5}Si\textsubscript{2.4}Ge\textsubscript{1.6}.\textsuperscript{11,12,40} The low-temperature low-resistivity states of the former group of specimens is conventional since the low-temperature orthorhombic phase is ordered ferromagnetically and has a higher symmetry than the high temperature paramagnetic monoclinic phase, thus corresponding to a less disordered state and reduced scattering. On the other hand, the low-temperature high-resistivity behavior of the polycrystalline Gd\textsubscript{5}Si\textsubscript{1.95}Ge\textsubscript{2.05} was observed to be metastable,\textsuperscript{12} \textit{i.e.}, after cycling through the first-order phase transformation about 20 times via either changing the temperature or magnetic field, the electrical resistivity of this compound showed a low-temperature low-electrical-resistivity behavior, similar to those of Gd\textsubscript{5}Si\textsubscript{1.8}Ge\textsubscript{2.2} and Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{2}. The change of the nature of the electrical resistivity transformation was explained by postulating a redistribution of the Si and Ge atoms in the behavior of the Gd\textsubscript{5}Si\textsubscript{1.95}Ge\textsubscript{2.05} compound after cycling through the first-order phase crystal lattice and a twin boundary migration in the high temperature monoclinic phase.
After the first two measurements shown in Figure 5.1, the same sample of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ was cycled through the first-order phase transformation by changing the temperature between 5 and 300 K in a zero magnetic field, or by varying magnetic field between 0 and 40 kOe isothermally between 105 and 130 K. The total number of cycles was 30. Unfortunately, the sample broke during the last cycle and it was sitting at room temperature for 21 months. Then, the largest remaining piece of this sample with dimensions of 1.88×0.98×0.44 mm$^3$ was used for the following study of the electrical resistivity along the $a$-axis. Figure 5.2 shows the temperature variation of the electrical resistivity of this smaller sample in zero and 40 kOe magnetic fields. The value of the resistivity at 5 K (first data point of this data set) substantially decreases from the measurement of the cycled sample, see Figure 5.1, which may come from two possible reasons. The first one is that the microcracks were mostly contained in the discarded part of the sample (which is unlikely). And the second one is that long time room temperature “anneal” results in a substantial relief of the stress with time.

The low-temperature high-resistivity behavior along the $a$-axis of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal does not change in the remaining part of the original sample after cycling and room temperature “anneal”, which is different from that of the Gd$_5$Si$_{1.95}$Ge$_{2.05}$ compound.$^{12}$

![Figure 5.2. Temperature ($T$) dependencies of the electrical resistivity ($\rho$) of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal measured upon heating (solid symbols) and cooling (open symbols) between 5 and 320 K in zero (circles) and 40 kOe (triangles) magnetic fields ($H$). Both $H$ and 10 mA electrical current ($I$) were applied along the $a$-axis of the crystal. The sample was cycled through the first-order phase transformation for 30 times and then “annealed” at room temperature for 21 months. The measurements in 40 kOe magnetic fields were carried out after the measurements of zero magnetic field $\rho(T)$ and the isothermal $\rho(H)$ measurements shown in Figure 5.4. The arrows indicate the directions of the temperature variation.](image-url)
suggesting that different mechanisms may be involved. *In-situ* x-ray powder diffraction study of a ground Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal presented in Chapter 3 demonstrated coexistence of a major orthorhombic phase and a minor monoclinic phase at 5 K, where 20 mol.% of the monoclinic phase was observed. This concentration remains nearly constant up to 100 K. Above the crystallographic phase transformation temperature (117 K upon zero field heating), the sample is a pure monoclinic phase. Given that the scattering of the conduction electrons by interphase boundaries between the orthorhombic and monoclinic phases may add a significant additional contribution to the electrical resistivity compared to a high temperature pure monoclinic phase state, the low-temperature high-resistivity and high-temperature low-resistivity of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along the *a*-axis may be qualitatively explained.

Note that these interphase boundaries do not cause additional scattering of conduction electrons traveling along the *b*- and *c*-axes, which will be explained below. Thus, similar electrical resistivity behaviors of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along its *a*-axis and polycrystalline Gd$_5$Si$_{1.95}$Ge$_{2.05}$ at their first-order phase transformations have different origins, resulting in different behaviors after cycling. Moreover, relative changes of the values of the electrical resistivity during the phase transformation in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along its *a*-axis reach 98% and 92% upon heating and cooling in a zero magnetic field, respectively. These values are much greater than 20% change observed in the Gd$_5$Si$_{1.95}$Ge$_{2.05}$ compound during its first-order phase transformation upon heating and cooling. Note that all of the values listed above were corrected by subtracting the temperature independent residual resistivity (approximately taken as the resistivity at 5 K for each cycle), which increases substantially when the sample is cycled through the first-order phase transformation due to increasing internal stresses and possibly due to formation of microcracks.
The large low-temperature resistivity, its persistence after cycling, and the large changes at the first-order phase transformation of observed along the $\alpha$-axis indicate that scattering of the conduction electrons by microstructural features due to an intrinsic phase coexistence$^{78}$ may dominate all other contributions to the electrical resistivity below the first-order phase transformation temperature. Such a substantial increase of electrical resistivity upon cooling through a first-order phase transformation to a crystallographic phase coexistence state has been reported in the case of incomplete martensitic phase transformation in the rare earth intermetallic compound GdCu. Here, about a 100% rise of electrical resistivity was observed in the region where the high-temperature cubic austenite and the low-temperature orthorhombic martensite phases coexist at a length scale of $10^2$ to $10^3$ $\mu$m.$^{100}$ It is worth mentioning that such intrinsic phase coexistence of martensites and austenites down to low temperatures was also observed in alkali metals, and it is in agreement with Landau theory.$^{101,102}$

The low-temperature high-resistivity was also observed in other systems undergoing martensitic phase transformations, such as ferromagnetic shape memory alloys Ni-Mn-Ga,$^{103-105}$ Ni-Fe-Ga,$^{106}$ Ni-Fe-Al,$^{107}$ and Ni-Mn-In$^{108}$ in the vicinity of their first-order crystallographic phase transformations between a low-temperature low-symmetry martensite and a high-temperature high-symmetry austenite phases. Twin variants were formed in martensites to accommodate elastic strain upon the phase transformations, resulting in a high electrical resistivity at the low temperature martensite phase. Indeed, first-order transformations in the $R_5(Si_xGe_{1-x})_4$ family, including the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ compound, are martensitic-like proceeding via sheer displacement of the subnano-thick slabs in the $ac$ plane of the unit cell. However, twinning occurs in the high-temperature, low-symmetry monoclinic phase,$^{21}$ which should lead to the high-temperature high-electrical-resistivity
behavior. Therefore, the low-temperature high-resistivity behavior of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along its $a$-axis does not originate from twinning in the monoclinic phase, which is different from the above mentioned shape memory alloys.

Figure 5.1 and Figure 5.2 also show that 20 and 40 kOe magnetic fields applied along the $a$-axis of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal shift the first-order phase transformation temperature from the zero field transformation temperature by 8±1 and 16±1 K, respectively. This together with large change of the electrical resistivity during the first-order phase transformation, results in very high values of magnetoresistance in the vicinity of the phase transformation, as shown in Figure 5.3. For example, when $T = 126$ K is reached upon heating in a zero magnetic field, the sample is in the monoclinic phase with $\rho$ (0 kOe, 126 K) = 22 $\mu$Ω cm, after $\rho_0 = \rho$ (0 kOe, 5 K) has been subtracted. On the other hand, when $T = 126$ K is reached by heating in a 20 kOe magnetic field, the sample is in a phase separated state with a much higher electrical resistivity, $\rho$ (20 kOe, 126 K) = 2615 $\mu$Ω cm.

To eliminate the stress build-up effect, $\rho(0,T)$ was then normalized by adding the difference between the zero and 20 kOe fields resistivities at 5 K and at the temperature right before the paramagnetic to ferromagnetic transition, for temperatures below and above the phase transition, respectively. This results in high values of MR, ~200%, at the vicinity of the first-order phase transformation. Because the stress is partially self annealed during the cooling process, the resistivity difference at 5 K is an underestimate of the effect over the whole ferromagnetic temperature range. This underestimation results in an artificial positive MR in the ferromagnetic state along the $a$-axis shown in Figure 5.3. When this artificial contribution is subtracted from the peak MR, a true peak MR value becomes close to 150%, which is the same as that obtained in a direct measurement, as seen in Figure 5.4.
Figure 5.3. Temperature dependency of the magnetoresistance with the magnetic field and electrical current ($I$) applied along the $a$-axis of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal, calculated from the data plotted in Figure 5.1.

Obviously, the MR ratio with the 20 kOe magnetic field applied along the $a$-axis of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal is much different in the vicinity of first-order phase transformation from that of a normal ferromagnet, where a few percent MR usually originates from a reduction of the electron-magnon scattering. It has been reported that in some doped LaMnO$_3$ compounds, the crystallographic transformation temperature and Curie temperature may coincide and the structural phase transformation can be induced by an applied magnetic field. As a result, the CMR effect in these compounds may reach $\sim$100\%.$^{47}$ Since in a $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal, an external magnetic field greater than 10 kOe applied along its $a$-axis can trigger a simultaneous first-order magnetic order-disorder and crystallographic phase transformation (see Chapter 3), the origin of the CMR effect observed in the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal along the $a$-axis may also be related to a strong coupling between magnetism and the lattice.

5.2. Isothermal magnetoresistance along the $a$-axis

To further explore the behavior of the magnetoresistance of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal along the $a$-axis, measurements of the isothermal electrical resistivity under applied magnetic
field between zero and 40 kOe were carried out at selected temperatures. The magnetoresistance as a function of applied magnetic field is shown in Figure 5.4. At temperatures below and well above 117 K, which is the first-order phase transformation temperature taken as the temperature at the peak of the electrical resistivity upon heating in a zero magnetic field, the magnetoresistance is weak and typical of a conventional ferromagnet and paramagnet, respectively. Small negative values of the magnetoresistance manifest reduction of the electron-magnon scatterings by the external magnetic field. Noticeable hysteresis between magnetic field increasing and decreasing branches at and below 114 K may be assigned to magnetic domains. Notably, the 5 and 50 K curves show changes of their curvatures at 38 and 20 kOe, respectively, which coincide with the second-order spin

![Graph showing isothermal magnetic field dependency of magnetoresistance at selected temperatures measured with the magnetic field and electrical current applied along the a-axis of the Tb₅Si₂.2Ge₁.8 single crystal. The arrows mark the direction of the magnetic field change. The top panel shows the MR below ~ 120 K and well above ~ 120 K (a), while the lower panel shows the MR close to the phase transition during the first, second and thirtieth cycles (b).]
reorientation transitions determined from dc magnetization data shown in Chapter 3. In these transitions, the magnitudes of the magnetoresistance and magnetization both increase with increasing magnetic fields, indicating the magnetic origin of these magnetoresistance anomalies.

Starting from 119 K, the magnetoresistance along the $a$-axis of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal becomes positive and reaches about 160% because of a first-order phase transformation. Approximately 14 kOe hysteresis is observed between field increasing and decreasing branches. The critical magnetic fields where the magnetoresistance rises (drops) rapidly coincide with those for the first-order phase transition between the paramagnetic and ferromagnetic phases at the same temperatures (see Chapter 3), indicating same origin of the abrupt changes of the magnetic states and electrical resistivities. The isothermal magnetization data between 119 and 136 K with the magnetic field applied along the $a$-axis of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal showed that increasing external magnetic field leads to a first-order transition from a paramagnetic to a ferromagnetic state. Normally this should result in a decrease of the electrical resistivity from the electron-magnon scattering contribution. Therefore, the observed drastic increase of the electrical resistivity should be assigned to the magnetic-field-induced crystallographic phase transformation. The ferromagnetic phase with a high electrical resistivity state is a mixture of the orthorhombic and monoclinic phases, and the paramagnetic phase with a low electrical resistivity state is a pure monoclinic phase.

Among known low-temperature high-resistivity shape memory and R$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys, the isothermal magnetic field dependencies of the electrical resistivity were reported for only two compounds. The magnetoresistance is -80% for a Ni-Mn-In alloy under a 100 kOe magnetic
field,\textsuperscript{108} and it is +16\% for the polycrystalline Gd\textsubscript{5}Si\textsubscript{1.5}Ge\textsubscript{2.5} under various temperature dependent critical magnetic fields less than 40 kOe.\textsuperscript{11} However, there are no data for the magnetic field dependency of the electrical resistivity after cycling through the first-order phase transformations, even though it is well-known that phase coexistence states generally result from complicated energy landscapes, and metastability is common in such systems manifesting itself as temperature or magnetic field history dependent physical properties. Thus, it is meaningful to conduct cycling experiments, results of which are shown in Figure 5.4(b). With cycling, the values of the magnetoresistance drop from 150\% to 90\% from the first to the second cycle, and then continue to drop reaching 20\% at the 30\textsuperscript{th} cycle, meanwhile the sign of the magnetoresistance remains positive. The always positive magnetoresistance indicates the persistence of the coupling of the magnetic ordered state and the crystallographic phase coexistence during isothermal cycling. The great decrease of the magnitude of the magnetoresistance upon cycling can be directly related to a substantial increase of the zero field resistivity at 122 K from \textasciitilde950 \textmu\Omega cm at the first cycle to \textasciitilde7800 \textmu\Omega cm at the 30\textsuperscript{th} cycle. And this phenomenon can be explained by the irreversibility of the magnetic field induced crystallographic phase transformation. If the amount of magnetic field induced orthorhombic phase increases upon cycling, the volume content of the interphase boundaries will increase; therefore, leading to the observed increase of the zero magnetic field electrical resistivity. This postulation is supported by the \textit{in-situ} x-ray powder diffraction study of the Tb\textsubscript{5}Si\textsubscript{2.2}Ge\textsubscript{1.8} compound (see Figure 5.5), which illustrates that the orthorhombic phase concentration increases during three cycles upon isothermally varying magnetic field at 2 K above $T_C$. The data in Figure 5.5 were collected using the same \textit{in-situ} x-ray powder diffraction sample and experiment methods and instruments as in Chapter 3.
Figure 5.5. Isothermal magnetic field dependences of the concentration of the orthorhombic phase of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ at 2 K above its Curie temperature ($T_C$), which was determined from the Rietveld refinement of the x-ray powder diffraction patterns upon increasing and decreasing the applied magnetic field. The first set of data (open circles) was measured after thermal demagnetization of the sample to 230 K and then cooling down to a temperature of 2 K above $T_C$. And the second (solid triangles) and third (solid circles) sets of data were then measured successively. The magnetic field was changed in 2 kOe steps between zero and 40 kOe. The arrows indicate the directions of the magnetic field change.

5.3. Temperature dependencies of the electrical resistivity along the $b$ and $c$-axes

Generally, the electrical resistivity is anisotropic for a single crystal of a non-cubic metal because the conduction electron paths are different along different directions in the crystal lattices of such metals, thus leading to different scattering phenomena. Therefore, the electrical resistivity behavior with the current flowing along different crystallographic axes of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal is expected to be different.

The temperature dependencies of the electrical resistivity along the $b$- and $c$-axes of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal between 5 and 200 K are shown in Figure 5.6 and Figure 5.7, respectively. Because no anomalies were observed between 200 and 320 K, these data are not shown in the figures for clarity. In a zero magnetic field, first order phase transformations, manifested as 73% and 81% discontinuous increases of the electrical resistivities along the $b$- and $c$-axes, respectively, occur at temperatures close to that observed along the $a$-axis.

Magnitudes of hystereses for all three axes are also similar. The 20 kOe applied magnetic field does not change the values of the phase transformation temperature, hysteresis, and electrical resistivity along the $b$-axis (Figure 5.6). Consequently, the resulting
magnetoresistance with 20 kOe magnetic field applied along the b-axis is negligible. Notably, the change of the residual resistivity along the b-axis upon thermal cycling is nearly negligible, and is the smallest compared to the other two axes of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal (we note that the a- and b-axes samples came from the same piece of single crystal). This is likely because the first-order crystallographic phase transformations are via movements of the slabs in the ac plane of the crystal lattice, building up internal stress in this plane, which increases the residual resistivity substantially.

![Figure 5.6](image1.png)

**Figure 5.6.** Temperature (T) dependencies of the electrical resistivity (ρ) of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal measured upon heating (solid symbols) and cooling (open symbols) between 5 and 200 K in zero (circles) and 20 kOe (triangles) magnetic fields (H). Both H and the 10 mA electrical current (I) were applied along the b-axis of the crystal. The arrows indicate the directions of the temperature variation.

![Figure 5.7](image2.png)

**Figure 5.7.** Temperature (T) dependencies of the electrical resistivity (ρ) of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal measured upon heating (solid symbols) and cooling (open symbols) between 5 and 200 K in zero (circles) and 20 kOe (triangles) magnetic fields (H). Both H and the 10 mA electrical current (I) were applied along the c-axis of the crystal. The arrows indicate the directions of the temperature variation.
Another major difference among the temperature dependencies of the electrical resistivity along the three major crystallographic directions of the \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) single crystal is that a 20 kOe magnetic field applied along the \( b \)- and \( c \)-axes does not change the first-order phase transformation temperature, but does so along the \( a \)-axis (see Figure 5.1, Figure 5.6 and Figure 5.7). This phenomenon is in line with the crystallographic and metamagnetism study of the \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) compound described in Chapter 3, showing that a magnetic field with a magnitude of 20 kOe applied along the \( a \)-axis direction could drive a coupled magnetic and crystallographic phase transformation via strong magnetoelastic interactions, but not along the \( b \)- and \( c \)-axes.

Obviously, the electrical resistivities along the \( b \)- and \( c \)-axes exhibit a low-temperature low-resistivity behavior, distinctly different from that along the \( a \)-axis, indicating that the interphase boundaries between the orthorhombic and monoclinic phases do not give rise to a noticeable increase of scattering of conduction electrons moving along the \( b \)- and \( c \)-axes directions. In the \( \text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8} \) crystal lattices the monoclinic structure is a distorted orthorhombic structure via a cooperative shear movement of the adjacent layers along the \( a \)-axis in opposite directions by \( \sim 0.2 \) Å (see Chapter 3). Thus, interphase boundaries mentioned above should be located between the \( bc \) planes of the two adjacent orthorhombic and monoclinic domains, as illustrated in Figure 5.8. Consequently, only the conduction electrons moving along the \( a \)-axis direction will encounter the scattering by disorders due to the mismatch at interphase boundaries; those along the \( b \)- and \( c \)-axes directions, on the contrary, will not be affected by these boundaries.

This explanation is further supported by the comparison among the values of resistivities along the three principle crystallographic directions. The virgin curves of the temperature
dependencies of the electrical resistivity show a much greater electrical resistivity along the \textit{a}-axis than those along the \textit{b}- and \textit{c}-axes; for example, at 5 K they are 300, 75, and 42 \(\mu\Omega\) cm for the \textit{a}-, \textit{b}- and \textit{c}-axes, respectively. Since the low temperature electrical resistivity generally comes from impurities and static lattice imperfections, and the \textit{a}- and \textit{b}-axes samples are from the same single crystal, the substantially greater resistivity value along the \textit{a}-axis may due to the orthorhombic and monoclinic interphase boundaries. It is worth mentioning that the low-temperature low-resistivity behavior along the \textit{b}- and \textit{c}-axes of the \textit{Tb}_{5}\text{Si}_{2.2}\text{Ge}_{1.8} single crystal is consistent with other members in the \textit{R}_{5}(\text{Si}_{x}\text{Ge}_{1-x})_{4} family, such as polycrystalline \textit{Gd}_{5}\text{Si}_{1.8}\text{Ge}_{2.2} and \textit{Gd}_{5}\text{Si}_{2}\text{Ge}_{2},^{9,10} where phase coexistence state was reported only in the vicinity of the first-order phase transformation, and the high and low temperature phases were considered to be pure phases. Since the lower symmetry in the high temperature monoclinic phase of these compounds corresponds to a more disordered state than the low temperature orthorhombic phase, together with the twinning microstructures observed in this phase, it reasonably exhibits a higher electrical resistivity.

Figure 5.8. Two-dimensional schematic of the \textit{ab} planes of (A) the orthorhombic and (B) monoclinic phases of \textit{Tb}_{5}\text{Si}_{2.2}\text{Ge}_{1.8}. The dashed lines delineate the domains of the major phases in each case. The \textit{c}-axis is normal to the plane of the figure and is marked as a solid dot. The length scale of domains is generally less than 10 nm,\textsuperscript{109} and they are shown in identical sizes only for simplicity. The solid lines in (A) indicate the domains of the minor monoclinic phase retained in the phase separated state.
5.4. Isothermal magnetoresistance along the $b$ and $c$-axes

The longitudinal magnetoresistance of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along the $b$-axis is shown in Figure 5.9. The positive magnetoresistance at 5 and 40 K is in line with the antiparallel configuration of the $b$-axis projection of the magnetic moments of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound at this temperature range. A simultaneous decrease and increase of spin fluctuations of the moments parallel and antiparallel to the applied magnetic field, respectively, leads to a net increase of the electrical resistivity upon the increase of the external magnetic field, which was established both experimentally and theoretically for antiferromagnetic metals.$^{110,111}$ The magnetic field dependency of the magnetoresistance in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal along the $b$-axis does not show a conventional $MR \propto H^2$ relationship as in a normal antiferromagnetic metal. This is understandable considering the complex non-collinear magnetic structure of the compound.

The magnitudes of the magnetoresistance decrease with increased temperature, which is likely due to the increase of the zero magnetic field electrical resistance because the elevated temperature enhances both the electron-phonon and electron-magnon scatterings.
Interestingly, the magnetoresistance becomes negative at temperatures above 68 K even though the $b$-axis projections of the magnetic moments remain antiparallel to each other. The change of the sign of the magnetoresistance is related to a temperature-induced second-order magnetic phase transition that occurs at 68 K. Above the first-order phase transition temperature, the longitudinal magnetoresistance along the $b$-axis is negative and decreases with increased temperature, which is normal for the paramagnetic state of the compound. Note that there is almost no hysteresis of the longitudinal magnetoresistance along the $b$-axis between magnetic field increase and decrease processes.

Figure 5.10 shows the longitudinal magnetoresistance with the magnetic field applied along the $c$-axis of the $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ single crystal. The magnetoresistance is negative between 5 and 95 K, see Figure 5.10(a). A near saturation behavior is observed at 5 K, typical for a ferromagnet and in agreement with the observation of the $c$-axis projections of the magnetic moment being parallel at this temperature. Interestingly, the magnetoresistance increases with increasing temperature from 5 to 40 K, and then decreases from 40 to 114 K. Hystereses upon magnetic field increase and decrease were observed between 5 and 95 K, with a maximum value at 70 K.

According to the neutron diffraction study, the magnetic moments are turning away from the $c$- to the $a$-axis in zero magnetic field upon increasing temperature from 5 to 70 K, and eventually develop an antiparallel configuration of the $c$-axis projections of the moments between 70 K and the magnetic order-disorder transition temperature, which result from the competition among RKKY exchange, magnetocrystalline anisotropy, and thermal energy. Applying external magnetic fields leads to new arrangements of magnetic moments and atoms, therefore, giving rise to the variations of the longitudinal magnetoresistance along the
c-axis. The magnetoresistance shows several anomalies near the zero-magnetic-field first-order phase transformation temperature, 117 K. The magnetizing curves show positive magnetoresistance between 115 and 117 K, and the demagnetizing curves are positive for 117 K but negative for 115 and 116 K, see Figure 5.10(b). And magnetoresistance at 118 K and temperatures immediately above shows the typical behavior of a ferromagnet, see Figure 5.10(c), which possibly comes from the short-range ferromagnetic correlations in this regime.

Figure 5.10. The isothermal magnetic field dependencies of the magnetoresistance at selected temperatures measured with the applied magnetic field and electrical current along the c-axis of the Tb$_{5}$Si$_{2.2}$Ge$_{1.8}$ single crystal. The magnetizing curves start from the zero points. The arrows indicate the directions of the magnetic field change.
CHAPTER 6. Spontaneous Generation of Voltage in Single Crystal

Gd$_5$Si$_2$Ge$_2$, Tb$_5$Si$_2$Ge$_{1.8}$, and Gd

6.1. Spontaneous generation of voltage in single crystal Gd$_5$Si$_2$Ge$_2$

The SGV signals collected from a Gd$_5$Si$_2$Ge$_2$ single crystal sample along the $a$-axis direction as functions of temperature and the rate of temperature change in a zero magnetic field are displayed in Figure 6.1. The characteristics of the temperature induced SGV signals are similar for all three samples, so they are not shown here for conciseness. The onset temperatures of the SGV signals are located within 2 K of the Curie temperature ($T_C$) derived from the dc magnetization measured in a 1 kOe field using the same sample, which are 269 K and 259 K for warming and cooling, respectively, confirming that the origin of the SGV is the coupled magnetic and crystallographic phase transformation. A thermal hysteresis of about 10 K of the SGV signals is observed, in good agreement with the first order nature of the transformation.

![Figure 6.1](image)

All signals are S-shaped, starting at $T_C$, falling to a minimum, and then increasing rapidly to a maximum, finally ending at temperatures 2 to 4 K higher or lower than $T_C$ upon heating or
cooling, respectively. Although the shapes of the SGV signals remain unchanged, a higher temperature sweep rate increases the magnitude of the SGV signal, and raises or lowers the temperature at which the SGV signal appears upon heating or cooling, respectively. The shapes of the SGV signals are quite similar to the thermal emf signals observed during the freezing of water, the melting of tin, and the solidification and the two polymorphic transformations of CuBr, suggesting that a similar mechanism may be responsible for these signals.\(^{112}\)

Figure 6.2 shows the isothermal SGV signals induced by sweeping the magnetic field at a rate of \(\sim 40\) kOe/min in the single crystal samples along three principal crystallographic directions and in a polycrystalline sample. The purpose of using the polycrystalline sample is to verify previous observations and to compare them with the single crystal samples. The polycrystalline sample had the dimensions of \(6.57 \times 2.48 \times 1.85\) mm\(^3\).

In order to illustrate how the SGV signal relates to the magnetic field induced phase transformation, the isothermal dc magnetization data measured at the same temperatures are also shown in Figure 6.2. Because there are compositional differences in different single
crystal samples (see Ref. 16 for details), the temperatures were normalized to the individual $T_c$’s determined for each specimen from low field dc magnetization. It is clear that the onsets and offsets of the SGV signals triggered by magnetic fields coincide, respectively, with the rapid increase of the magnetization and its saturation due to the magnetic field induced phase transitions between the paramagnetic and ferromagnetic states. Upon field increasing, the SGV signal starts at the onset of the PM to FM transition, reaches a maximum and then drops to a minimum, finally goes back to zero when the magnetic transition is complete. Upon field decreasing, the shape of the SGV signals does not change much, with a maximum appearing first, followed by a minimum. The onset and end points of the SGV signals occur at lower fields during demagnetizing than during magnetizing, which is normal for a first order phase transformation. The magnetic fields of the onsets and, especially of the ends of the SGV signals are slightly different for different crystallographic directions, demonstrating weak anisotropy, as expected considering the layered and highly anisotropic crystal structure of Gd$_5$Si$_2$Ge$_2$.

The shapes of the SGV signals are similar for $b$- and $c$-axes direction samples when subjected to a same variation of a same trigger (temperature or magnetic field), while that of the $a$-axis direction sample seems unique. As it is known from the structural characterization of the Gd$_5$Si$_2$Ge$_2$, the shear movement of the slabs during the coupled magnetostructural phase transformation occurs along the $a$-axis, and this is likely the reason for the uniqueness of the SGV behavior of the a-axis sample. There is a small difference in the magnitudes of the SGV signals for the single crystal samples along different crystallographic directions. Since the magnitude of the SGV signal depends on the sample shape and the distance between the two electrical connections to the sample, this small difference in the magnitudes is extrinsic. The magnitudes of the SGV signals for the polycrystalline sample, however, are about three times
smaller than those of the single crystal samples despite similar shapes and locations of the electrical connections to the samples. Thus, a smaller SGV signal in a polycrystal is intrinsic. This feature correlates well with the fact that the first-order transitions in single crystal samples are usually sharper than those in polycrystalline samples of the same composition, and it is in line with the results from the magnetic force microscopy and thermal expansion studies of a Gd$_5$Si$_2$Ge$_2$ single crystal.$^{113}$

As mentioned above, the higher temperature sweep rate increases the magnitude of the SGV signal. For the magnetic field induced SGV signals, the increase of the rate of change of the stimulus also increases the magnitude of the signal, as shown in Figure 6.3(a). The critical field, at which the SGV signal starts, also exhibits a systematic change with changing the magnetic field sweep rate. As shown in Figure 6.3(b), the increased field sweep rate shifts the critical field to lower values for all the samples. This is in line with an earlier observation that the critical field of the magnetostructural transition in Gd$_5$Ge$_4$ is also field sweep rate
There are some differences in the absolute values of the magnitudes of the signals and the values of the $\Delta H_C = H_C - H_C@1\text{kOe/min}$ for different samples, but they may be extrinsic for different single crystal samples. The difference between the polycrystalline and single crystal samples is intrinsic due to the reasons mentioned above.

The main reason for the SGV was thought to be the Seebeck effect, given the similarity of the SGV profile and the signal recorded from a differential thermocouple simultaneously. A compositional difference or/and a temperature difference on the two ends of the sample triggers the phase transformation from one specific end, propagating to another. The heat release or absorption during this process gives rise to the S-shape and polarity change of the SGV signal when the direction of temperature or/and magnetic field change is reversed. It is worth noting, however, that when a sample is flipped without reversing the polarity of the electrical connections, the polarity of the SGV signal also reverses. This behavior supports the notion that there is a small gradient of composition along the sample, and therefore a slight change of the $T_C$, because a temperature gradient caused by the instrument should always be the same, regardless of how the sample is mounted.

6.2. Spontaneous generation of voltage in single crystal $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$

As shown in Figure 6.4, temperature induced SGV appears along all three major crystal axes of $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ between 110 and 118 K, where the crystallographic and magnetic phase transformations occur (see Ref. 35 and Chapters 3 and 4). The SGV starting temperatures are different upon heating and cooling by $\sim 5$ K. This separation is nearly the same as the extent of thermal hysteresis of the crystallographic phase transformation (see Chapters 3 and 4). Therefore, one can associate the SGV with the crystallographic transformation. Figure 6.4 also shows that the SGV increases with the increased rate of temperature change, which is
Figure 6.4. The SGV of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ as a function of temperature measured along the $a$-, $b$-, and $c$-axes upon heating and cooling at various rates in a zero magnetic field.

Figure 6.5. The SGV of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ as a function of magnetic field applied along the $a$-, $b$-, and $c$-axes at 120 K. The field change rate is ~40 kOe/min. The arrows mark the directions of the magnetic field changes.
similar to that observed in Gd$_5$Si$_2$Ge$_2$. On the other hand, a magnetic field of 40 kOe and lower can trigger the SGV only when the field vector is parallel to the $a$-axis. A representative result at 120 K is displayed in Figure 6.5. This observation is different from Gd$_5$Si$_2$Ge$_2$, where the SGV occurs when a magnetic field is isothermally applied along any of the three major crystallographic directions in the vicinity of $T_C$.

Both neutron and x-ray powder diffraction studies of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ illustrate a temperature induced first-order crystallographic phase transformation involving a large unit cell volume change of ~1% (Ref. 35 and Chapter 3). By rearranging the Clausius-Clapeyron equation$^{115}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad \text{to} \quad \Delta H = T \frac{dP}{dT} \Delta V,$$

where $P$, $T$, $S$, $V$, and $H$ are the pressure, temperature, entropy, volume, and enthalpy, respectively, it is obvious that the enthalpy change, i.e. latent heat, is proportional to the unit cell volume change. The latent heat in turn determines the temperature gradient across the sample when its crystallographic phase transformation starts from one end of the specimen and then propagates to another. Since temperature is a scalar, the appearance of SGV does not depend on the orientations of the samples. Therefore, temperature induced SGV appears along all three major crystal axes, and depends on the latent heat of the first-order phase transformation.

The anisotropy of the magnetic field induced SGV in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is in line with its highly anisotropic metamagnetism and magnetocaloric effect (MCE) (Chapter 3). Both the PM$\leftrightarrow$FM metamagnetism and GMCE occur only with $H||a$ when $H \leq 40$ kOe (Chapter 3). The absence of SGV with $H||b$ and $H||c$ when $H \leq 40$ kOe (Figure 6.5) confirms that it is the
magnetocaloric effect that is responsible for the temperature gradients necessary for the observation of the field induced SGV.

6.3. Spontaneous generation of voltage in single crystal Gd

The roles played by latent heat and MCE in SGV were further studied by using a single crystal of Gd metal. No SGV occurs in the vicinity of $T_C = 293$ K as long as the magnetic field remains constant. Since the phase transition at $T_C$ is a pure second order magnetic one, no latent heat is involved here. The absence of SGV in the elemental Gd near $T_C$ supports the notion that the temperature induced SGV depends on the latent heat of the first-order phase transformation.

The SGV in Gd can, however, be triggered by applying a magnetic field isothermally in the vicinity of $T_C$. Figure 6.6 exhibits the SGV of Gd as a function of magnetic field applied along the $c$-axis between 278 and 304 K with a field increasing at the rate of $\sim 40$ kOe/min. The largest magnitude of SGV, which is taken as the voltage difference between the positive and negative peaks, is $\sim 2 \mu$V. It is observed at 294 K, i.e. in the immediate vicinity of the maximum MCE, which occurs at 293 K. This is much smaller than the SGV of Gd$_5$Si$_2$Ge$_2$ and Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystals (see Figure 6.2 and Figure 6.5). This is consistent with the behavior of the MCE in Gd, which decreases gradually as the temperature is further away from $T_C$, (see Ref. 116), the magnitude of the SGV signal exhibits a similar reduction with temperature as is clearly seen in Figure 6.6. Furthermore, since the thermoelectric signal is proportional to the temperature difference ($\Delta T$) between two ends of a specimen, and Gd$_5$Si$_2$Ge$_2$ and Tb$_5$Si$_{2.2}$Ge$_{1.8}$ have a greater MCE compared to that of Gd, one concludes that the MCE determines $\Delta T$, and therefore, determines the magnitude of the magnetic field induced SGV.
Figure 6.6. The SGV of Gd as a function of magnetic field applied along the $c$-axis at constant temperatures between 278 and 304 K. The measurements were carried out with field increasing at a rate of ~40 kOe/min.
CHAPTER 7. Conclusions

First-order magnetic-field-induced metamagnetic-like transitions were observed in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal with the field parallel to the $a$- and $c$-axes, but not for the $b$-axis. Consequently, the giant magnetocaloric effect has been observed when the field is parallel to the $a$- and $c$-axes. In-situ x-ray powder diffraction measurements of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ showed that the crystallographic phase transformation between the O(I) and M phases is strongly influenced by the applied magnetic field, indicating the strong magnetoelastic coupling.

Applying a magnetic field less than 40 kOe isothermally just above the $T_C$ of a powder sample of Tb$_5$Si$_{2.2}$Ge$_{1.8}$ cannot drive either the crystallographic or the magnetic phase transformation to completion; and the O(I) phase concentration changes concurrently with the bulk magnetization of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ powder subjected to an applied magnetic field. These observations indicate that the metamagnetic-like transition above $T_C$ in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ is of magnetoelastic origin; and the magnetic and structural phase transitions become coupled in magnetic field greater than ~10 kOe applied a few Kelvin above the zero magnetic field $T_C$.

The magnetocrystalline anisotropy plays an important role in these transitions, and accounts for the unusual features found in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ material.

The ordering temperatures and thermal hystereses of the magnetic order-disorder transition in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ are highly anisotropic when an applied magnetic field reaches and exceeds 10 kOe. The temperature-induced spin reorientation transition occurring at ~70 K in a zero magnetic field is clearly observed from $M(T)$ data collected with fields below 10 kOe applied along all three principal crystallographic axes. It becomes less visible and shifts to lower temperatures with $H||b$, or becomes undetectable with $H||a$ and $H||c$ in a 50 kOe external
field. Field-induced magnetic phase transitions have been observed between 1.8 and 70 K with $H||a$ and $H||b$, but not $H||c$.

The anisotropic Griffiths phase-like behavior has been observed above $T_C$ in the temperature dependencies of magnetization measured in 10, 100, and 1000 kOe magnetic fields. Below ~150 K and above $T_C$, the magnetic susceptibility exponent exhibits the largest negative deviation from unity when $H||a$. The anisotropy of the Griffiths-like phase behavior originates from anisotropic ferromagnetic short-range order when $T_C < T < ~150$ K. The anomalous separation of the heating and cooling magnetization curves observed in low applied magnetic fields in this temperature range is most persistent with the magnetic field applied along the $b$-axis.

Anomalies in thermal history dependencies of magnetization above $T_C$ confirm the decoupling of the magnetic and crystallographic phase transformations. A model involving magnetic domain effects in the long-range ordered state of the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compound has been proposed to explain anomalous thermal history in the vicinity of $T_C$. Strong magnetocrystalline anisotropy of the compound is reflected in the anisotropic field-temperature phase diagrams constructed for the three independent crystallographic directions.

The electrical resistivities of single crystal Tb$_5$Si$_{2.2}$Ge$_{1.8}$ along its $a$-, $b$- and $c$-axes as functions of temperature between 5 and 320 K and magnetic field between 0 and 40 kOe are presented. Positive colossal magnetoresistance (CMR) with a magnitude of 150% is observed in the Tb$_5$Si$_{2.2}$Ge$_{1.8}$ single crystal with magnetic field applied along the $a$-axis near the first-order magnetic and crystallographic phase transformations. The origin of the CMR effect is suggested to be an intrinsic crystallographic phase coexistence state.
While along the \(a\)-axis the low temperature resistivity below \(T_C\) is higher than that above \(T_C\), the electrical resistivities along the \(b\)- and \(c\)-axes of the \(\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}\) single crystal show low-temperature, low-resistivity behavior. This phenomenon has been explained by the geometry of the interphase boundaries between the low temperature major phase (orthorhombic) and the high temperature minor phase (monoclinic). The longitudinal magnetoresistance with magnetic fields less than 40 kOe applied along the \(b\)- and \(c\)-axes is less than 8 and 5%, respectively, \textit{i.e.} neither a CMR nor a GMR effect is observed for these two directions but MR reaches 150% along the \(a\)-axis.

The spontaneous generation of voltage in both single crystal and polycrystalline \(\text{Gd}_5\text{Si}_2\text{Ge}_2\) samples has been studied as a function of temperature, magnetic field, and the rates of their changes. The critical temperatures and magnetic fields at which the SGV signals appear nearly coincide with the Curie temperatures and the critical magnetic fields at which the first order magnetostructural phase transformations occur. This observation confirms the intimate relationship between the SGV and the coupled magnetic crystallographic phase transformation.

A weak anisotropy was observed in single crystal \(\text{Gd}_5\text{Si}_2\text{Ge}_2\) samples through their different SGV responses. The magnitude of the SGV signal clearly increases with the rate of the temperature and magnetic field change. The rate of stimuli changes also shifts the critical temperatures and critical magnetic fields. Although more research is needed to better map out the details of the SGV behavior in the \(\text{Gd}_5\text{Si}_2\text{Ge}_2\) alloy, it is a likely candidate for a smart miniature temperature and magnetic field sensor material for near room temperature applications, adding a new aspect of its potential manifold practical applications.
Temperature induced SGV has been observed in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ along three major crystallographic axes near $T_C$, but not in a Gd single crystal. This suggests that a phase transformation involving a large volume change, *i.e.* a large latent heat, is necessary for the temperature induced SGV. There is no obvious enhanced anisotropy in temperature induced SGV in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ compared to Gd$_5$Si$_2$Ge$_2$. The magnetic field induced SGV has been observed in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ near $T_C$ only with $H||a$, but not with $H||b$ and $H||c$ when $H \leq 40$ kOe. Thus, field induced SGV in Tb$_5$Si$_{2.2}$Ge$_{1.8}$ shows much stronger anisotropy compared to Gd$_5$Si$_2$Ge$_2$. The field induced SGV has also been observed in Gd near $T_C$. These observations indicate that a first-order magnetostructural phase transformation is not a necessary condition for SGV to occur. But a large MCE for the magnetic field induced SGV is necessary for the latter in order to be observed.
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REFERENCE

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APPENDIX. Reprints of published papers

Most of the results presented above have already been published. This appendix contains reprints of the following papers that are directly related to this thesis.

1. M. Zou, V. K. Pecharsky, K. A. Gschneidner, Jr., D. L. Schlagel and T. A. Lograsso,


Magnetic phase transitions and ferromagnetic short-range correlations in single-crystal Tb$_2$Si$_2$Ge$_{1.8}$

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Magnetic phase transitions in a Tb$_2$Si$_2$Ge$_{1.8}$ single crystal have been studied as a function of temperature and magnetic field. Magnetic-field dependencies of the critical temperatures are highly anisotropic for both the main magnetic ordering process occurring around 120 K and a spin reorientation transition at ~70 K. Magnetic-field-induced phase transitions occur with the magnetic field applied isothermally along the a and b axes (but not along the c axis) between 1.8 and 70 K in fields below 70 kOe. Strong anisotropic thermal irreversibility is observed in the Griffiths phase regime between 120 and 200 K with applied fields ranging from 10 to 1000 Oe. Our data (1) show that the magnetic and structural phase transitions around 120 K are narrowly decoupled; (2) uncover the anisotropy of ferromagnetic short-range order in the Griffiths phase; and (3) reveal some unusual magnetic domain effects in the long-range ordered state of the Tb$_2$Si$_2$Ge$_{1.8}$ compound. The temperature-magnetic field phase diagrams with field applied along the three major crystallographic directions have been constructed.

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I. INTRODUCTION

The $R_2$Si$_2$Ge$_{1.4}$ intermetallic compounds, where $R$ is a rare-earth element, were brought to the forefront of materials physics after the discovery of the giant magnetocaloric effect in Gd$_2$(Si$_2$Ge$_{1.4}$)$_4$. Other interesting phenomena, including the colossal magnetostriiction, giant magnetoresistance, and spontaneous generation of voltage, were observed in these alloys soon after. The unusually strong magnetoresponsiveness in the Gd$_2$(Si$_2$Ge$_{1.4}$)$_4$ systems is due to first-order magnetic martensitic-like transitions which can be triggered reversibly by temperature, magnetic field, and pressure.

The Tb$_2$(Si$_2$Ge$_{1.4}$)$_4$ system is the second most studied subset in the family of $R_2$Si$_2$Ge$_{1.4}$ alloys. The Tb-based compounds exhibit the giant magnetocaloric effect in the intermediate range of compositions, 0.35 < $x$ < 0.65. The crystallographic transformation in Tb$_2$(Si$_2$Ge$_{1.4}$)$_4$ between the monoclinic and orthorhombic polymorphs, and the magnetic ordering-disordering phase transition between the paramagnetic and canted ferromagnetic states (henceforth referred to as simply “ferromagnetic,” also see Fig. 1), which are different from Gd$_2$(Si$_2$Ge$_{1.4}$)$_4$, are decoupled by about 10 K and less than 5 K when $x$ = 0.5 and 0.55, respectively. Moreover, the separate crystallographic and magnetic phase transitions can be decoupled in a polycrystalline Tb$_2$Si$_2$Ge$_2$ by applying hydrostatic pressures greater than 8.6 kbar, or by magnetic fields greater than 10 kOe when applied along the easy magnetization direction, i.e., along the a axis, of the Tb$_2$Si$_2$Ge$_{1.8}$ single crystal. In either case, the compound transforms from the monoclinic paramagnetic to the orthorhombic ferromagnetic state. External magnetic fields up to 70 kOe applied along the magnetically hard direction, i.e., along the b axis of single crystalline Tb$_2$Si$_2$Ge$_{1.8}$, are not strong enough to induce the paramagnetic to ferromagnetic phase transition at temperatures slightly higher than the zero field $T_C$. However, fields between 60 and 70 kOe can trigger the paramagnetic to ferromagnetic transition when applied along the c axis.

Although a study of the field-induced magnetostructural transition of Tb$_2$Si$_2$Ge$_{1.8}$ has been reported, experimental data about the temperature-dependent behavior in different magnetic fields are lacking. Knowing the latter, however, is important because the decoupling of the magnetic and struc-

![FIG. 1. (Color online) Crystal and magnetic structures of Tb$_2$Si$_2$Ge$_{1.8}$ following Ref. 11. The left panel shows the magnetic structure between 75 and ~120 K and it also highlights the connectivity of the slabs via Tb1-T3-T2-Tb1 bonds. The top panel on the right shows the orientations of the magnetic moments of the Tb atoms in one slab between 75 and ~120 K. The bottom panel on the right shows the orientations of the magnetic moments in one slab below 75 K. T1, T2, and T3 represent a statistical mixture of Si and Ge atoms of the 2.2:1.8 (0.55:0.45) atomic ratio.](image-url)
tural phase transitions in Tb$_2$(Si$_x$Ge$_{1-x}$)$_4$ lead to a complicated crystallographic and magnetic phase coexistence near $T_c$. Furthermore, intrinsic twinning at the nanoscale in the monoclinic phase enhances the Griffiths-like phase behavior in polycrystalline Tb$_2$Si$_2$Ge$_2$, which is detected by the less-than-unity exponent of the inverse susceptibility in magnetic fields between 1 and 1500 Oe due to ferromagnetic short-range order. Anisotropic ferromagnetic short-range order has been observed in both antiferromagnetic and paramagnetic states of single crystal Gd$_2$Ge$_2$, and was ascribed to the anisotropy of the layered crystal structure of the Gd$_2$Ge$_4$ compound considering negligible single-ion anisotropy of Gd$^{3+}$. The anisotropy is expected to be much enhanced when $R$=Tb.

Another substantial difference between the magnetic properties of Tb$_2$(Si$_x$Ge$_{1-x}$)$_4$ and Gd$_2$(Si$_x$Ge$_{1-x}$)$_4$ in the intermediate range of compositions is the presence of spin reorientation transitions, which occur in Tb$_2$(Si$_x$Ge$_{1-x}$)$_4$ at $T_R$ = 70 K and 75 K when $x$=0.5 and 0.55, respectively, well below their magnetic order-disorder transformations at 780 K. The spin reorientation transitions separating two different ferromagnetic states in Tb$_2$(Si$_x$Ge$_{1-x}$)$_4$ are absent in Gd$_2$(Si$_x$Ge$_{1-x}$)$_4$. Below and above $T_R$, the magnetic structure remains canted ferromagnetically along the $a$ axis, but the moments tilt further away from the $a$ axis upon cooling as can be seen in Fig. 1. The antiferromagnetically aligned moment components along the $b$ axis vary insignificantly both in their directions and magnitudes during this spin reorientation transition. The $c$-axis components, however, change from antiferromagnetic above $T_R$ to a ferromagnetic alignment below $T_R$. There is no apparent crystallographic change associated with these spin reorientation transitions in either Tb$_2$Si$_2$Ge$_2$ or Tb$_2$Si$_2$Ge$_4$. According to the neutron-diffraction study of Tb$_2$Si$_2$Ge$_2$, the spontaneous magnetic moments of Tb atoms located in three inequivalent crystallographic sites have different canting angles, indicating different local magnetocrystalline anisotropy of Tb moments.

To carry out a systematic study of the magnitization of Tb$_2$Si$_2$Ge$_2$ single crystal measured by the tri-arc method and to further explore the anisotropy of the Griffiths phase behavior, the temperature and magnetic-field dependencies of the dc magnetization along the three principal crystallographic axes of a high-purity Tb$_2$Si$_2$Ge$_2$ single crystal are presented. Our results show a complicated magnetic behavior as a function of temperature, magnetic-field, and crystallographic directions. A strong anisotropy was observed in the Griffiths phase regime, and is likely responsible for the low-field (less than 1000 Oe) thermal history dependencies of the magnetization of the compound.

II. EXPERIMENTAL DETAILS

Tb$_2$Si$_2$Ge$_2$ single crystal for the magnetization measurements was grown by the tri-arc method from high-purity Tb, Si, and Ge mixed in appropriate quantities. The Tb was prepared by the Materials Preparation Center and contained the following major impurities (in ppm at.): O, 1900; C, 1100; N, 1800; F, 40; Cl, 33; thus it was approximately 99.67 at. % (99.97 wt. %) pure. The Si and Ge were purchased from Meldform Metals Ltd. and were better than 99.999 at. % pure. The as-grown crystal was oriented by using backscattered Laue x-ray diffraction. A sample for the magnetization measurements was cut by spark erosion. The sample was in the form of a parallelepiped with dimensions of $1.50 	imes 1.94 	imes 0.88$ mm$^3$ along the $a$, $b$, and $c$-axes directions, respectively, and weighed 18.73 mg.

The temperature ($T$) and magnetic-field ($H$) dependencies of the magnetization ($M$) were measured from 1.8 to 300 K in constant magnetic fields of 0.01, 0.1, 1, 10, and 50 kOe, and from 0 to 70 kOe at various constant temperatures ranging between 1.8 and 70 K in a superconducting quantum interference device (SQUID) magnetometer, MPMS-XL from Quantum Design, Inc. When measuring $M(T)$, three sets of data were collected for each fixed applied magnetic field and orientation of the single crystal. The first one was collected upon heating in a constant magnetic field applied at the lowest temperature after the sample was zero field cooled (ZFC) from a temperature well above its Curie temperature ($T_C$). The second and third ones were collected upon cooling and heating in the same field strength as that in the first, ZFC heating measurement. The first set of data is referred to as ZFC heating, the second as field-heated (FH) cooling, and the third one as field-cooled (FC) heating hereafter. Every isothermal $M(H)$ measurement was recorded after thermal demagnetization at 250 K and then zero field cooling down to the measurement temperature. The applied magnetic fields varied from 0 to 70 kOe with a 2 kOe step. The misalignment between the directions of the magnetic-field vector and the crystal axes was less than $\pm 5^\circ$, considering the combined accuracy of crystallographic alignment and sample positioning inside the cryostat.

III. RESULTS AND DISCUSSION

Temperature dependencies of the magnetization of single-crystal Tb$_2$Si$_2$Ge$_2$ measured in a 10 kOe magnetic field applied along the $a$, $b$, and $c$-axes directions between 1.8 and 200 K are shown in Fig. 2. The FC heating and FH cooling data overlap over the entire temperature range except for small differences at $T_C$, i.e., hysteresis along the $a$ and $c$ axes, and a spike along the $b$ axis. Thus, only ZFC heating and FH cooling data are displayed for clarity.

The $M(T)$ behaviors shown in Fig. 2 exhibit several noteworthy features. First, below $T_C=120$ K, the magnitudes of the magnetization with $H||a$ and $H||c$ are much greater than those with $H||b$. This is in line with the magnetic structure of this compound, where the magnetic moments are mainly confined to the $a$-$b$ plane (see Fig. 1). Second, a cusp in the $H||a$ and $H||b$ $M(T)$ curves, and a minimum in the first derivative of magnetization with respect to temperature ($dM/dT$) with $H||c$ (inset of Fig. 2) are consistent with a spin reorientation transition at $\sim 70$ K. With $H||a$, the magnetization increasing on heating from 2 to 70 K is in agreement with decreasing of the average angle that the Tb moments form with the $a$ axis from 38.4° at 4.2 K to 9.3° at 75 K. From 70 to about 120 K magnetization with $H||a$ shows a typical ferromagnetic behavior as the magnetic structure...
FIG. 2. (Color online) Temperature dependencies of the magnetization of single-crystal Tb$_5$Si$_3$Ge$_{14}$ measured in a 10 kOe magnetic field applied parallel to the $a$, $b$, and $c$ axes upon ZFC heating (open symbols) and FH cooling (solid symbols). The inset is the temperature dependence of the first derivative of the magnetization with respect to temperature $\frac{dM}{dT}$ when $H\parallel c$ upon FH cooling. Note that the temperature scale is the same for the three orientations.

Along the $a$ axis remains unchanged. The magnetic-moment component along the $c$ axis switches from a ferromagnetic to an antiferromagnetic configuration upon heating through 70 K. This corresponds to a change of the sign of $\frac{dM}{dT}$ when the magnetic field is parallel to the spin axis, i.e., the ferromagnetic susceptibility decreases, while an antiferromagnetic susceptibility increases upon heating. Consequently, $\frac{dM}{dT}$ minimum is formed at 70 K with $H\parallel c$.

When $H\parallel b$, the magnetization values initially decrease with increasing temperature from 1.8 K, form a minimum at about 40 K, and then reach a maximum at 70 K. Contrary to $H\parallel a$ and $H\parallel c$, this behavior does not follow the thermal evolution of the $b$-axis components of spontaneous magnetic moments in zero field. Recalling that measured magnetization also manifests the ability of the external field to overcome the magnetoelastic anisotropy energy, magnetoelastic energy, and thermal fluctuations to align the moments in the field direction, the complicated thermal variation of the magnetization with $H\parallel b$ may reflect the thermal dependence of the magnetic anisotropy energy. When 70 K < $T$ < ~120 K, the magnetization with $H\parallel b$ continuously decreases upon heating. Upon FH cooling, however, a sharp spike develops at 118 K. The explanation of the physical origin of this singularity will be given below during the discussion of the low-field temperature dependencies of the magnetization of Tb$_5$Si$_3$Ge$_{14}$.

The magnetic order-disorder transition, which occurs around 120 K, shows a thermal hysteresis of 4 K when $H\parallel a$ and $H\parallel c$, which signifies a first-order phase transition, but the hysteretic behavior is different when $H\parallel b$. In the $R_5(Si,Ge)_{14}$ family with $R$ = Gd, the first-order magnetic order-disorder transition is always a coupled magnetic and crystallographic phase transition. For example, in Gd$_5$Si$_3$Ge$_2$ compound, which is analogous to Tb$_5$Si$_3$Ge$_{14}$, the transformation from a high-temperature monoclinic to a low-temperature orthorhombic phase is accompanied by a paramagnetic to ferromagnetic transition. In Tb$_5$Si$_3$Ge$_{14}$, however, these two transitions (magnetic and crystallographic) may be decoupled, and the extent of decoupling is composition dependent. Since decoupling in Tb$_5$Si$_3$Ge$_{14}$ is less than 5 K, and the two transitions can be decoupled by applying $H$ = 10 kOe when $H\parallel a$, the magnetic order-disorder transitions shown in Fig. 2 with $H\parallel a$ and $H\parallel c$ are likely coupled magnetostuctural phase transformations. The difference in hysteretic behavior when $H\parallel b$ is due to the fact that the 10 kOe magnetic field is not strong enough to align the moments in the field direction. This explanation is consistent with temperature dependencies of the magnetization measured in a 50 kOe applied magnetic field, which are shown in Fig. 3. Only ZFC heating and FH cooling results are displayed here because the ZFC and FC heating data are identical.

From Fig. 3, one can see that the magnetic order-disorder transitions exhibit very similar thermal hysteresis regardless of the direction of the 50 kOe magnetic field. The magnitudes of the magnetization at temperatures immediately below the ferromagnetic to paramagnetic transition are equivalent to 6.7 $\mu_B$, 3.1 $\mu_B$, and 5.1 $\mu_B$ per Tb atom with $H\parallel a$, $H\parallel b$, and $H\parallel c$, respectively. Taking the value with $H\parallel a$ as a reference, the relative collinearity of the magnetic moments with applied magnetic field is 100%, 47%, and 76% with $H\parallel a$, $H\parallel b$, and $H\parallel c$, respectively. Similarity of hysteretic behaviors shown in Fig. 3 with those observed in numerous Gd$_5$(Si,Ge)$_{14}$ compounds indicates that when a sufficient fraction of magnetic moments is aligned with the external field, the magnetic order-disorder transition in Tb$_5$Si$_3$Ge$_{14}$ becomes first-order and is likely a coupled magnetic and crystallographic phase transition. The transition takes place at different temperatures when the 50 kOe magnetic field is applied along different directions. Consistent with the relative collinearity of the moments, the transition temperature is
the highest with \( H_{\text{II}\alpha} \), the lowest with \( H_{\text{II}b} \), and it is intermediate with \( H_{\text{II}c} \). This is expected because states with greater disorder (\( H_{\text{II}b} \) and \( H_{\text{II}c} \)) can be destroyed by lower thermal energy. Moreover, wider hysteresis is associated with lower magnetic ordering temperatures when \( H_{\text{II}b} \) \((-6\) K\) and \( H_{\text{II}c} \) \((-5\) K\) compared to \(-4\) K when \( H_{\text{II}a} \). The hysteresis generally arises from the need to overcome some energy barriers separating neighboring low energy states, which in this case, is mainly due to the crystallographic phase transition. As the transition temperature lowers, the widening hysteresis reflects complexity of the energy landscape in TbSb\(_2\)Se\(_4\).

Figure 3 also shows that the spin reorientation transition either shifts to lower temperature in a 50 kOe magnetic field (\( H_{\text{II}b} \)) or becomes indistinguishable (\( H_{\text{II}a} \) and \( H_{\text{II}c} \)) when compared to the 10 kOe data of Fig. 2. This is expected because at \( T_{\text{SR}} \), the orientations of Tb moments changes within the \( ac \) plane, and applying higher magnetic field within the same plane is more effective in aligning the moments. Consequently, \( T_{\text{SR}} \) becomes indistinguishable when the moments remain mostly aligned with the 50 kOe field regardless of temperature as long as it remains below \( T_{\text{C}} \).

The significant difference between the temperature dependence of the magnetization with 10 and 50 kOe external fields applied parallel to the three principal crystallographic axes indicates a complicated thermal evolution of the magnetic structure of TbSb\(_2\)Se\(_4\) in the presence of external magnetic fields. This may be further probed by measuring magnetization isotherms at different temperatures with magnetic field applied along the three major crystal axes.

Figure 4 shows the magnetization isotherms of the \( \text{TbSb}_2\text{Se}_4 \) single crystal measured at 1.8 K. The magnetization with \( \text{IIa} \) involves a two-step process. The first step corresponds to the domain-wall movement when the applied field is increased from 0 to 6 kOe and it then continues as a slow increase of the magnetization due to a coherent rotation of magnetic moments toward the direction of the applied field from 8 to 38 kOe. Two facts are noted: (i) no hysteresis occurs when the applied field is greater than 10 kOe, and (ii) the magnetization at \( H = 10\) kOe is \( 7.4\mu_B \) per Tb atom, which is close to the value of the average \( \alpha \) axis component (\( 7.3\mu_B \) per Tb atom) obtained from the neutron-diffraction study. Hence, from 10 to 38 kOe, the material is a single domain with a major ferromagnetic component of all magnetic moments along the \( \alpha \) axis (see Fig. 1). Note, that at this point the magnetic moments in the domain have substantial canting angles with the \( \alpha \) axis. The second step of magnetization starts with a rapid increase when the applied field is between 40 and 48 kOe, indicating that the magnetic structure of \( \text{TbSb}_2\text{Se}_4 \) has changed. This step brings a nearly full alignment of moments along the external field direction because the magnetization value at \( H = 48\) kOe is \( 9.3\mu_B \) per Tb atom, close to the \( 9.4\mu_B \) per Tb atom obtained from the neutron-diffraction measurements at 4.2 K, and to the theoretically expected value of \( gJ = 9\mu_B \). The excess of \( 0.3\mu_B \) reflects contributions from itinerant 5d electrons of Tb. There is only a narrow hysteresis associated with this magnetic phase transition.

Since the magnetic moments are mainly confined to the \( ac \) plane of the \( \text{TbSb}_2\text{Se}_4 \) crystal lattice, the nearly linear increase of the magnetization upon increasing the applied field from 0 to 46 kOe in the \( b \)-axis direction is due to a continuous rotation of the magnetic moments toward the external field direction. This rotation is reversible, and consequently, there is no hysteresis. A discontinuous increase by \( 1.9\mu_B \) per Tb atom occurs between 46 and 50 kOe. This discontinuity indicates a sudden change of the orientation of some of the magnetic moments when the external field overcomes the anisotropy energy. We argue that this field-induced magnetic phase transition is a result of flipping the moments at the \( \text{TbI}1 \) sites (see Fig. 1) out of the \( ac \) plane and becoming parallel to the \( b \) axis. Recall that the \( \text{TbI}1 \) moments are perpendicular to the \( b \) axis in a zero magnetic field. Of the \( \text{Tb} \) sites in the \( \text{SnS}_2\text{Ge}_4 \)-type structure, 20% are \( \text{TbI}1 \) sites and the remaining 80% are equally divided between \( \text{TbI}2 \) and \( \text{TbI}3 \). Thus, flipping all \( \text{TbI}1 \) moments from perpendicular to parallel to the external field, should suddenly increase magnetization by \( 20\% \) of the full magnetic moment of the Tb atom (\( 9.3\mu_B \times 20\% = 1.9\mu_B \)). A hysteresis of about 2 kOe accompanies this transition, which also indicates a strong magnetoelastic effect.

Although the magnetic moments are mainly confined to the \( ac \) plane, the magnetization at 1.8 K with \( H_{\alpha} \) shows quite different features from that with \( H_{\text{II}a} \). First, there is a hysteresis between the field increasing and decreasing branches over the entire range of fields, suggesting that besides being dominant during the initial magnetization process between 0 and 6 kOe, the domain-wall movements accompany the coherent magnetic-moment rotation between 8 and 70 kOe. Second, the magnitude of the magnetization at \( H = 10\) kOe, equivalent to \( 5.2\mu_B/\text{TbI}^1 \), is only slightly smaller than \( 5.5\mu_B \) the \( \alpha \)-axis component of the spontaneous magnetization at 4.2 K. These two observations mean that the material is close to but not completely in a single domain state when the applied field is greater than 10 kOe and applied in the \( \alpha \)-axis direction. Therefore, domain walls are not as mobile when \( H_{\alpha} \) when compared to \( H_{\text{II}a} \). Consequently, a smaller remanent magnetization mainly due to domain-wall pinning is observed with \( H_{\alpha} \) than with \( H_{\text{II}a} \). Third, the absence of magnetization jumps, such as those observed with \( H_{\text{II}a} \) between 40 and 48 kOe, and with \( H_{\text{II}b} \) between 46
and 50 kOe, indicates that there is no field-induced magnetic phase transition below 70 kOe with \( H_{1c} \). This is in line with the neutron-diffraction observation\(^4\) that the Tb moment projection along the \( c \) axis is ferromagnetic at low temperature.

The magnetic phase transitions that occur at 1.8 K when the magnetic field is applied along the \( a \)- and \( b \)-axis directions result from a competition between the magnetocrystalline anisotropy and the external field. Since the magnetocrystalline anisotropy generally varies with temperature, it is reasonable to expect such transitions to occur at different critical magnetic fields as temperature varies. When the system reaches the spin reorientation temperature, \( T_{SR} \approx 70 \) K, the magnetic moments are almost collinear in the \( a \)-axis direction, therefore, the magnetic field applied in this direction needed to induce the magnetic phase transition isothermally should be lower. This is indeed the case when the magnetization of the TbSi_2Ge_8 single crystal was measured isothermally as a function of applied magnetic field between 1.8 and 70 K, representative isotherms at 10, 40, and 70 K are shown in Fig. 5. The values of the critical fields decrease with increasing temperature, indicating a reduction of the magnetocrystalline anisotropy energy. The magnetization steps during the field-induced transitions also decrease with increasing temperature from \( \approx 0.8 \mu_B \) at 10 K to \( \approx 0.3 \mu_B \) at 40 K to zero at 70 K, reasonably closely following the decrease of tilting angles of magnetic moments with the \( a \)-axis. The field-induced transition along the \( b \)-axis also disappears at \( T_{SR} \approx 70 \) K. The magnetization at 70 kOe and 70 K is 4.3\( \mu_B \), which is close to that at 70 kOe and 40 K (4.9\( \mu_B \)). Therefore, the absence of a sharp field-induced transition along the \( b \)-axis at and above 70 K indicates that the Tb moments are coherently rotated from the \( ac \) plane to the \( b \)-axis upon the increasing of the external magnetic field.

The magnetization isotherms with the applied field along the \( c \)-axis direction show a departure from the ferromagnetic behavior with increasing temperature, which is consistent with the tilting of the magnetic moments away from this direction when temperature increases from 1.8 to 70 K. No field-induced magnetic phase transition with \( H_{1c} \) is observed in Fig. 5. Therefore, between 1.8 and 70 K, the field-induced magnetic phase transitions occur with \( H_{1a} \) and \( H_{1b} \), but not with \( H_{1c} \) when the magnetic field is less than 70 kOe. On the contrary, when temperatures are in the vicinity of or above the \( T_C \) of TbSi_2Ge_8, field-induced magnetic phase transitions occur when the external field is along the \( a \) and \( c \) axes directions but not the \( b \)-axis (see Figs. 1 and 2 in Ref. 13). This difference suggests a strong thermal variation of the magnetic anisotropy energy.

Figure 6 illustrates the temperature dependencies of the inverse dc magnetic susceptibilities \( (H/M) \) of TbSi_2Ge_8 measured during FC heating from 1.8 to 300 K with a 10 Oe magnetic field applied along the \( a \), \( b \), and \( c \) axes. The Griffiths phase-like behavior is evident by a characteristic negative deviation\(^9\) from the Curie-Weiss behavior and less-than-hexagonality magnetic-susceptibility exponents\(^20\) between \( T_C \) (118 ± 2 K) and \( T_{SR} \). The latter is the critical Griffiths temperature of 200 ± 2 K as marked in Fig. 6, taken as the temperature where the \( H/M \) curves start deviating from the Curie-Weiss behavior. The inset of Fig. 6 shows the logarithmic representation of the main panel data \( (H/M \text{ vs } T) \) and their fitting to the relation \( \chi^{-1} \alpha(T-T_C)^{-\lambda-1} \), where \( T_C \) is an adjustable parameter, and \( \lambda \) is the magnetic-susceptibility exponent parameter. In the conventional paramagnetic phase.

\[ \chi^{-1} \alpha(T-T_C)^{-\lambda-1} \]
above $T_C$, $\lambda_{PM}$ is zero and isotropic. In the Griffiths phase regime between $T_{PM}$ and $T_C$, both the negative deviations and $\lambda_{PM}$ are anisotropic. The most pronounced negative deviation and the largest $\alpha$ are found when the magnetic field is parallel to the $a$ axis, which is the magnetic easy axis at temperatures below $T_C$. This observation is in line with the report that in single crystal Gd$_2$Ge$_4$, the magnetic susceptibility along its easy magnetization direction always exhibits a greater deviation from Curie-Weiss behavior when compared to the other two major crystallographic directions below its $T_C$. The observed anisotropy is reasonable considering that the Griffiths-like phase originates from a system of ferromagnetic clusters in the paramagnetic phases of both single-crystal Gd$_2$Ge$_4$ and polycrystalline Tb$_2$Si$_2$Ge$_4$.\textsuperscript{15,16}

It is interesting to note that the differences in Weiss temperatures are consistent with the current understanding of the nature of magnetic exchange interactions in the family of $R_2T_4$ compounds, where $T$ is Si or Ge. It is known that the -RT-TR-network plays a significant role in defining magnetic interactions.\textsuperscript{21,22} Within each slab, the network of strongly interacting-Tbl-Tl-2T2-Tbl-atoms is two dimensional and it remains intact in both the paramagnetic and magnetically ordered states. The three dimensionality of the network is restored only in the magnetically ordered state when the monoclinic phase transforms into the orthorhombic Tb$_2$Si$_2$Ge$_4\text{\_}8$ in which the -Tbl-T3-T3-Tbl-network also exists (it is absent on the monoclinic phase where T3-T3 bonds are too long). Hence, strong pseudo-two-dimensional interactions in the planes of the slabs (ac plane) are reflected in the higher Weiss temperatures for $H||a$ and $H||c$.

The anisotropy of the ferromagnetic clusters in the Griffiths phase-like state of Tb$_2$Si$_2$Ge$_4\text{\_}8$ is also evident from the thermal history dependence of the dc magnetization measured in a 10 Oe applied magnetic field when $T_C< T<150$ K, Fig. 7. Here, the magnitude of magnetization is substantially greater when $T_C$ is approached than upon heating. This difference is greater the closer the system is to $T_C$. The resulting inverse thermal hysteresis, which is in contrast to a conventional thermal hysteresis where the magnetization measured at the same temperature upon heating is greater than that upon cooling (see Fig. 3), occurs because the magnetic and crystallographic phase transitions in the Tb$_2$Si$_2$Ge$_4\text{\_}8$ compound are decoupled by less than 5 K in zero and weak applied magnetic fields. Thus, the magnetic ordering on cooling starts with the ferromagnetic ordering of the monoclinic phase.\textsuperscript{10} This second order, purely magnetic phase transition, is preceded by growth of both the size and number of the monoclinic ferromagnetic clusters, which is responsible for the rapid increase of the magnetization when the temperature approaches 117 K from $T>T_C$ (Fig. 7). The drastic decrease of the magnetization from 117 to 115 K when $H||a$ and $H||b$ may be understood if one assumes that the crystallographic phase transition from the monoclinic to orthorhombic phase occurs over this temperature range. It has been established both theoretically\textsuperscript{24} and experimentally\textsuperscript{18} that in the closely related $R_2T_4$ compounds with $R$=Gd, the Curie temperature of the orthorhombic Gd$_2$Si$_4$-type polymorph is much higher than that of the monoclinic Gd$_2$Si$_4$-type phase. By analogy, and also considering preliminary theoretical modeling results,\textsuperscript{14} the orthorhombic Tb$_2$Si$_2$Ge$_4\text{\_}8$ has a higher $T_C$ when compared to the monoclinic Tb$_2$Si$_2$Ge$_4\text{\_}8$. This, on cooling to 115 K much of the monoclinic ferromagnetic Tb$_2$Si$_2$Ge$_4\text{\_}8$ single crystal transforms to the orthorhombic ferromagnetic structure, and $T_C$ of the latter is considerably greater than 115 K. Given that anisotropy constants generally increase when temperature is below $T_C$ and considering a strong single-ion anisotropy of the Tb$^{3+}$ ion, the anisotropy energy of the orthorhombic ferromagnetic Tb$_2$Si$_2$Ge$_4\text{\_}8$ is expected to be much greater than that of the monoclinic ferromagnetic Tb$_2$Si$_2$Ge$_4\text{\_}8$ at 115 K. Obviously, the orthorhombic magnetic domains form concurrently with the crystallographic phase transformation. Yet, a 10 Oe field is not large enough to move the domain walls of the orthorhombic ferromagnetic Tb$_2$Si$_2$Ge$_4\text{\_}8$ at 115 K. This leads to an abrupt decrease of the magnetization values upon cooling through the crystallographic phase-transition temperature. On heating, the structural transition is shifted by 4 to 5 K toward higher temperature,\textsuperscript{15} but the $T_C$ of the monoclinic phase remains the same, and overall, the transition is between the orthorhombic ferromagnetic and the monoclinic paramagnetic polymorphs of Tb$_2$Si$_2$Ge$_4\text{\_}8$. As a result, the magnetization values measured on heating are lower than those during cooling.

This model of the anomalous thermal hysteresis in Tb$_2$Si$_2$Ge$_4\text{\_}8$ when $T_C< T<150$ K is supported by the following observations. First, the inverse hysteresis disappears along the $a$ and $c$ axes when the field is increased to 1000 Oe, as shown in Fig. 8, indicating that coercive fields along these two directions are lower than 1000 Oe. Second, the thermal history dependencies of the magnetization in a 100 Oe magnetic field (see Fig. 9) applied along the $a$ and $c$ axes show a crossover behavior between the 10 and 1000 Oe field data. Finally, the thermal irreversibility near $T_C$ remains unconventional and abnormal along the $b$ axis even in fields as
FIG. 8. (Color online) Temperature dependencies of the magnetization of single-crystal Tb$_2$Si$_2$Ge$_4$ measured in a 1000 Oe magnetic field applied parallel to the $a$, $b$, and $c$ axes upon FC heating (open symbols) and FH cooling (solid symbols). Note that the temperature scale is the same for the three orientations.

The larger magnitude of magnetization upon FH cooling compared to PC heating in small magnetic fields (but not the sharp drop during cooling as in Tb$_2$Si$_2$Ge$_{1.8}$) has also been observed in a Gd$_2$Ge$_4$ single crystal. It was ascribed to short-range ferromagnetic correlations in both the paramagnetic and antiferromagnetic phases of the compound. These short-range ferromagnetic correlations originate from a competition between the interlayer and intralayer magnetic exchange interactions. In the Tb$_2$Si$_2$Ge$_{1.8}$ compound, the anomalous hysteresis away from $T_c$ is of a similar origin as the one in the Gd$_2$Ge$_4$ compound, but it is more persistent hysteresis anomaly along the $b$ axis.

FIG. 9. (Color online) Temperature dependencies of the magnetization of single-crystal Tb$_2$Si$_2$Ge$_{1.8}$ measured in a 100 Oe magnetic field applied parallel to the $a$, $b$, and $c$ axes upon FC heating (open symbols) and FH cooling (solid symbols). Note that the temperature scale is the same for the three orientations.

FIG. 10. (Color online) The temperature-magnetic-field phase diagrams with field applied along the $a$, $b$, and $c$ axes of Tb$_2$Si$_2$Ge$_{1.8}$. The solid and open circles represent critical temperatures from isofield $M(T)$ data upon ZFC heating and FH cooling, respectively; the solid and open triangles represent critical magnetic fields derived from the isothermal $M(H)$ data upon field increasing and decreasing, respectively. The solid and open diamonds in (a) represent the midpoints of the crystallographic phase transformations derived from the in situ x-ray powder diffraction data of Ref. 13. Panel (d) illustrates the Griffiths phase boundary derived from the low-field $M(T)$ data with $H||c$. The lines are guides to the eye. Arrows placed between the boundaries indicate phase separated regions for the corresponding directions of the temperature and magnetic field changes.
the decoupling of the magnetic and crystallographic phase transitions that defines the anomalous behavior of the magnetization in the immediate vicinity of $T_C$.

Conventional hysteresis occurring at $T_\text{C}$ when the 1000 Oe magnetic field is applied along the $a$ and $c$ axes has two factors in its origin. First, with increasing external field, the contribution from ferromagnetic clusters (Griffiths phase) becomes less visible (is quenched) due to an increased contribution from the paramagnetic matrix. Second, at $T/T_\text{C}$ the net magnetization increases because the external field exceeding the coercive field increases the volume of the domains with spins oriented in the direction favored by the external field. At $T_\text{C}$, the magnetization from ferromagnetic monoclinic Tb$_3$Si$_2$Ge$_4$ is no longer greater than that from the oriented magnetic domains of the orthorhombic phase of the compound, therefore, normal hysteresis corresponding to a first-order magnetic phase transition sets in. Obviously, this critical field should be markedly different along different crystallographic directions due to strong magnetocrystalline anisotropy below $T_\text{C}$. The persistence of the inverse hysteresis at 10 kOe applied along the magnetic hard $b$ axis is the manifestation of this mechanism.

Based upon the magnetization data from the present and previous studies, the magnetic phase diagrams of Tb$_3$Si$_2$Ge$_4$ with the magnetic field applied along the three major crystallographic directions are constructed and displayed in Fig. 10. It is worth mentioning that the $M(H)$ and $M(T)$ data are in excellent agreement with one another. The magnetically ordered phases are denoted as FM for the canted ferromagnetic structure observed in a zero magnetic field between $T_\text{SR}$ and $T_\text{C}$ and SR-FM for a different canted ferromagnetic structure, which is observed in a zero field below $T_\text{SR}$. The phase boundaries separating SR-FM and FM states with $\mathbf{H}||a$ and $\mathbf{H}||b$ closely follow one another, but they do not coincide. A similar phase boundary when $\mathbf{H}||c$ cannot be traced using $M(H)$ behavior because no obvious field-induced phase transition is observed here. These phase diagrams show a strong anisotropic behavior of the magnetic order-disorder transitions. Phase boundaries between the paramagnetic (PM) and magnetically ordered states for the three directions are considerably different from each other. For instance, magnetic field applied along the $a$ axis has a strong effect on $T_\text{C}$ ($dT_\text{C}/dH$ approaches 0.4 K/Oe). On the other hand, when the field is applied along the $b$ and $c$ axes, $dT_\text{C}/dH$ is lower by a factor of 4 to 5.

IV. CONCLUSIONS

The ordering temperatures and thermal hysterizes of the magnetic order-disorder transition in Tb$_3$Si$_2$Ge$_4$ are highly anisotropic when an applied magnetic field reaches and exceeds 10 kOe. The temperature-induced spin reorientation transition occurring at $\sim 70$ K in a zero magnetic field is clearly observed from $M(T)$ data collected with fields below 10 kOe applied along all three principal crystallographic axes. It becomes less visible and shifts to lower temperatures with $\mathbf{H}||b$, or becomes undetectable with $\mathbf{H}||a$ and $\mathbf{H}||c$ in a 50 kOe external field. Field-induced magnetic phase transitions have been observed between 1.8 and 70 K with $\mathbf{H}||a$ and $\mathbf{H}||b$, but not $\mathbf{H}||c$.

The anisotropic Griffiths phase-like behavior has been observed above $T_\text{C}$ in the temperature dependencies of magnetization measured in 10, 100, and 1000 kOe magnetic fields. Below $\sim 150$ K and above $T_\text{C}$ the magnetic susceptibility exponent exhibits the largest negative deviation from unity when $\mathbf{H}||a$. The anisotropy of the Griffiths-like phase behavior originates from anisotropic ferromagnetic short-range order when $T/T_\text{C}$ $\sim 150$. The anomalous separation of the heating and cooling magnetization curves observed in low applied magnetic fields in this temperature range is most persistent with the magnetic field applied along the $b$ axis. Anomalies in thermal history dependencies of magnetization above $T_\text{C}$ confirm the decoupling of the magnetic and crystallographic phase transformations. A model involving magnetic domain effects in the long-range ordered state of the Tb$_3$Si$_2$Ge$_4$ compound has been proposed to explain anomalous thermal history in the vicinity of $T_\text{C}$. Strong magnetocrystalline anisotropy of the compound is reflected in the anisotropic field-temperature phase diagrams constructed for the three independent crystallographic directions.

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Crystallography, anisotropic metamagnetism, and magnetocaloric effect in Tb$_{2}$Si$_{2-x}$Ge$_{x+1.8}$

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The metamagnetic-like transitions and giant magnetocaloric effect were observed with the magnetic field applied parallel to the a and c axes, but not the b axis in a Tb$_{2}$Si$_{2-x}$Ge$_{x+1.8}$ single crystal. The in situ x-ray powder diffraction study indicates that these metamagnetic-like transitions are coupled to crystallographic phase transformations occurring via strong magnetoelastic interactions. The magneto-crystalline anisotropy plays an important role in this system. Magnetic fields less than 40 kOe cannot drive either the magnetic or the crystallographic phase transition to completion for Tb$_{2}$Si$_{2-x}$Ge$_{x+1.8}$ powder due to the strong single ion anisotropy of Tb.

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INTRODUCTION

Over the last decade, magnetic materials with a large magnetocaloric effect are drawing increasing attention from the condensed matter community due to their potential applications in magnetic refrigeration.1-3 Many of these compounds exhibit magnetic-field-induced, first-order magnetic phase transitions which are believed to be responsible for the observed large magnetocaloric effect.4-7 For example, the Gd$_{2}$(Si$_{1}$Ge$_{0.7}$)$_{4}$ compounds show a strong magnetocaloric effect when they undergo coupled magnetostructural phase transitions, which is clearly evident from the concurrent change in the magnetization and crystal structure observed in Gd$_{2}$Ge$_{4}$ and related materials through bulk magnetization and in situ x-ray powder diffraction studies.8-9 One of the largest magnetocaloric effects near room temperature was reported in Gd$_{2}$(Si$_{1}$Ge$_{0.7}$)$_{4}$ in the intermediate composition range (x=0.5), where the compound changes its crystal structure from the monoclinic polymorph to the orthorhombic form during ferromagnetic ordering that can be triggered by either a lowering temperature,10 increasing magnetic field,11,12 or hydrostatic pressure.13,14

Above its Curie temperature ($T_C$), applying a magnetic field transforms the compound from the paramagnetic (PM) to the ferromagnetic (FM) state,15,16 during which the magnetic field dependence of the isothermal magnetization resembles that of a metamagnetic phase transition in an antiferromagnet. Therefore, these field-induced PM to FM transitions in Gd$_{2}$(Si$_{1}$Ge$_{0.7}$)$_{4}$ are also referred to as metamagnetic-like transitions.

The Tb$_{2}$(Si$_{1}$Ge$_{0.7}$)$_{4}$ compounds also exhibit the giant magnetocaloric effect in the intermediate composition range, around x=0.5.17 Initially, the origin of this phenomenon was assigned to the coupled magnetostructural phase transformation,18 the same as in Gd$_{2}$(Si$_{1}$Ge$_{0.7}$)$_{4}$ near x=0.5. However, unlike in Gd$_{2}$Si$_{2}$Ge$_{4}$, no clear metamagnetic-like behavior was observed in the magnetization of polycrystalline Tb$_{2}$Si$_{2}$Ge$_{4}$ and a follow-up neutron powder diffraction study of this compound revealed a decoupling of the structural and magnetic transitions with a separation of ~10 K.19 This was the first report indicating that the monoclinic structure may support long-range ferromagnetic order in the $R_2$(Si$_{1}$Ge$_{0.7}$)$_{4}$ family, where $R$ is a rare earth element. Interestingly, the magnetic and structural transitions in Tb$_{2}$Si$_{2}$Ge$_{4}$ can be recoupled by a hydrostatic pressure at and above 8.6 kbar, consequently enhancing the magnetocaloric effect of the compound by nearly 40% for a magnetic field change from 0 to 50 kOe.20 However, a recent neutron diffraction study of Tb$_{2}$Si$_{2}$Ge$_{4}$ single crystal indicated that decoupling of the magnetic and crystallographic transitions at this composition, if any, must be smaller than ~5 K.21 Given the fact that no intermediate magnetic-only transition of the monoclinic phase was detected within 5 K of the crystallographic transition in Tb$_{2}$Si$_{2}$Ge$_{4}$ (x=0.5), not only the separation of the magnetic and crystallographic transitions is smaller than the ~10 K reported for Tb$_{2}$Si$_{2}$Ge$_{4}$ (x=0.5) in
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Refs. 19 and 20, but the extent of the decoupling appears to change with concentration (x).

To facilitate a better understanding of the relationships between the magnetism and crystalllography in the Tb_{3}Si_{12}Ge_{18} system, and the origin of the large magnetocaloric effect, we have conducted dc magnetization and in situ x-ray powder diffraction studies of Tb_{3}Si_{12}Ge_{18}. Both single-crystal and powdered specimens were examined in the vicinity of T_{C} to seek structure-property information, the fine details of which may be masked by random orientation of the grains in polycrystalline samples.

EXPERIMENTAL DETAILS

The Tb_{3}Si_{12}Ge_{18} single crystal for the magnetization measurements was grown by the tri-arc method\textsuperscript{22} from high-purity Tb, Si, and Ge mixed in the appropriate amounts. This crystal was from the same batch that was used in the neutron scattering study by Garlea et al.\textsuperscript{21} The Tb was prepared by the Materials Preparation Center\textsuperscript{23} and contained the following major impurities (in ppm at.): O, 1,900; C, 1,100; N, 180; F, 40; Cl, 33; thus it was approximately 99.67 at. % (99.97 wt. %) pure. The Si and Ge were purchased from Meldrum Metals, Ltd., and were better than 99,999 wt. % pure. The as-grown crystal was oriented by using backscatter Laue x-ray diffraction and then a sample for the magnetization measurements was cut by spark erosion. The sample was a rectangular parallelepiped with dimensions of 1.50 $\times$ 1.94 $\times$ 0.88 mm$^3$ along the a, b, and c-axes directions, respectively, and weighed 18.73 mg. The temperature (T) and magnetic field (H) dependencies of magnetization were measured in a superconducting quantum interference device (SQUID) magnetometer MPMS-XL, manufactured by Quantum Design, Inc. The errors in the temperature, magnetic field, and magnetic moment were 0.5%, 1 Oe, and 1%, respectively. The SQUID is periodically calibrated to ensure that the magnetometer stays within these limits. Each isothermal M(H) measurement was recorded after thermal demagnetization at 230 K and then cooling down to the measurement temperature. The misorientation between the directions of the magnetic field vector and the crystal axes was less than $\pm$5°, considering the combined accuracy of crystallographic alignment and sample positioning inside the cryostat.

The sample used in the in situ x-ray powder diffraction measurements was ground from a different Tb_{3}Si_{12}Ge_{18} single crystal that was grown by the Bridgman method.\textsuperscript{24} The Tb used in this sample was prepared by the Materials Preparation Center\textsuperscript{23} and contained the following major impurities (in ppm at.): O, 1,500; F, 280; C, 230; Al, 130; Fe, 130; thus it was approximately 99.77 at. % (99.97 wt. %) pure. The Si and Ge were purchased from Meldrum Metals Ltd. and were better than 99,999 wt. % pure. The sample preparation, instrument setup, and the refinement method employed to process the in situ x-ray powder diffraction data were the same as in Refs. 8, 9, and 25. The temperature was stable within $\pm$0.02 K below 50 K and within $\pm$0.05 K above 50 K. The profile residuals were between 9 and 12%, and derived Bragg residuals were between 5 and 9%. Based on the least-squares standard deviations, the phase concentrations were determined with an error of less than 1%, and the interatomic distances were determined to within 0.01–0.03 Å. A sample to measure the magnetization as a function of the magnetic field was extracted from the specimen used to collect powder diffraction data in order to compare the two sets of measurements.

In order to address the coupling (or the separation) of the crystallographic and magnetic phase transitions, it is critical to determine the transition temperatures as precisely as possible. We used the Arrott plots\textsuperscript{26} method to determine the Curie temperatures (T_{C}) so as to avoid the effect of the magnetic-field-induced magnetization, which contrary to the spontaneous magnetization, may lead to considerable deviations from the material's true T_{C}. The internal magnetic field (H_{i}) inside the sample was used to construct the Arrott plots, and H_{i} was determined by subtracting the demagnetizing field from the applied field. The demagnetizing factor (N) was evaluated from the slope of the low-field linear regions of the M(H) curves in the ferromagnetic state.\textsuperscript{27} The determined values of N were consistent with the shape of the sample.

RESULTS AND DISCUSSION

The magnetization isotherms around T_{C} with the magnetic field applied parallel to the $a$ axis are shown in Fig. 1. The T_{C} determined from the isotherms using Arrott plots (inset of Fig. 1) is 118±1 K. This value is in good agreement with T_{C}=120 K reported in Ref. 21. At T=118 K, the field dependence of the magnetization is that of a typical ferromagnet, in agreement with the microscopic magnetic structure of...
\( \text{Crystrallography, Anisotropic Metamagnetism...} \)

Tb\(_{2}\)Si\(_2\)Ge\(_4\) determined by neutron diffraction.\(^{21}\) However, starting from \( T = 119 \) K (1 K above \( T_{C} \)) and at higher temperatures, the field dependence of the magnetization does not exhibit a normal paramagnetic behavior because a metamagnetic-like transition takes place. Upon increasing the magnetic field, an abrupt increase of the magnetization is observed at different temperature-dependent critical values of the field, leading the material to technical saturation. At 119 K and 70 kOe, the magnetic moment per Tb atom reaches 7.43 \( \mu_B \), which is close to the average magnetic moment per Tb atom at 100 K—7.58 \( \mu_B \)—determined from the neutron scattering study of polycrystalline Tb\(_{2}\)Si\(_2\)Ge\(_4\).\(^{21}\)

These field-induced magnetic transitions are reversible when \( T > 122 \) K, and they exhibit a large hysteresis (\(-15\) kOe) between the field increasing and decreasing branches. Two features—the abrupt change in the magnetization and the hysteresis—suggest that these transitions are of first order. The critical magnetic field (defined here as the field of the onset of the metamagnetic-like transition), \( H_{c,1} \), increases nearly linearly with the increasing temperature, which is quite similar to metamagnetic-like transitions observed in Gd\(_4\)(Si\(_2\)Ge\(_4\))\(_{2}\).\(^{15,16}\) However, when the magnetic field is parallel to the \( b \) and \( c \) axes (see Fig. 2), a much different behavior is observed. Fields under 70 kOe do not trigger a transition along the \( b \) axis, and the metamagnetic transition along the \( c \) axis exhibits different features when compared to that along the \( a \) axis, i.e., the transition along the \( a \) axis is much sharper [compare Figs. 1 and 2(b)]. Furthermore, the critical fields are by \(-36\) kOe higher along the \( c \) axis than along the \( a \) axis, and the rate of change of the \( H_{c,1} \) with temperature for the field parallel to the \( c \) axis (\( 5.4 \pm 0.3 \) kOe/K) is much larger than the same for the field parallel to the \( a \) axis (\( 2.64 \pm 0.22 \) kOe/K). The difference in the temperature dependence of the critical fields is discussed later. The magnetization isotherms below \( T_{C} \) (Fig. 2(c)) show that the \( a \) axis is the easy magnetization direction and the \( b \) axis is the hard one. This is fully consistent with the microscopic magnetic structure of Tb\(_{2}\)Si\(_2\)Ge\(_4\) in this temperature range, where a net ferromagnetic component of the magnetic moment is along the \( a \)-axis direction, the components along the \( b \) and \( c \) axes are correlated antiferromagnetically, and the moments are nearly confined in the \( ac \) plane.\(^{21}\)

The field-induced first-order magnetic transitions above \( T_{C} \) (i.e., in the paramagnetic state) are generally rare. As mentioned above, similar transitions were observed in both polycrystalline\(^{15}\) and single-crystal Gd\(_4\)(Si\(_2\)Ge\(_4\))\(_{2}\) along all three principal crystallographic directions;\(^{16}\) and they have been regarded as magnetoelastic transformations during which the magnetic and crystal structures change concurrently.\(^{7}\) According to a recent theoretical study of the electron correlation effects on the magnetostructural transition of Gd\(_4\)Si\(_2\)Ge\(_2\),\(^{20}\) the different polymorphs, i.e., the monoclinic and orthorhombic phases, have different \( T_{C} \)'s and, therefore, different temperature dependencies of the magnetization. Each of the two polymorphs should order magnetically via a conventional, second-order phase transition with \( T^{0}_{C} \) of the orthorhombic Gd\(_4\)Si\(_2\)Ge\(_2\) being considerably higher than the \( T^{0}_{C} \) of the monoclinic polymorph. The actual temperature of the magnetostructural transition of Gd\(_4\)Si\(_2\)Ge\(_2\), \( T_{C} \), is located between \( T^{0}_{C} \) and \( T^{N}_{C} \). Hence, when a magnetic field is applied just above \( T_{C} \), it changes the balance of the free energies between the paramagnetic monoclinic and ferromagnetic orthorhombic Gd\(_4\)Si\(_2\)Ge\(_2\) phases, which in turn triggers a crystallographic transition between two polymorphs that have different magnetizations, thus leading to a discontinuous change of the magnetization at \( H_{c,1} \). Given the fact that Tb\(_2\)(Si\(_2\)Ge\(_4\))\(_{1} x = 0.5 \) has the same sequence of polymorphs with the same types of crystal structures as Gd\(_4\)Si\(_2\)Ge\(_2\), the metamagnetic-like transitions in Tb\(_2\)Si\(_2\)Ge\(_4\) are likely to have the same mechanism. Since the single-ion anisotropy of Tb\(^{3+}\) is considerable when compared with the negligible single-ion anisotropy of Gd\(^{3+}\), a different contribution may further aid in the magnetic field dependence of a structural transition in Tb\(_2\)Si\(_2\)Ge\(_4\). Thus, magnetizing a material above \( T_{C} \) should induce a small but measurable magnetorstriction in a sample, resulting in a related strain that, in a way, may affect the sample similarly to an external pressure. In a polycrystalline sample, magnetic field-induced stress field should be quite complex and will be a function of the microstructure and preferred orientation.
but in a single crystal it may be approximated by a uniaxial pressure. Considering the strong dependence of the crystallographic-only transformation in Tb$_3$Si$_2$Ge$_2$ on hydrostatic pressure, the increased magnetic field, therefore, should be able to convert some or all of the large-volume monoclinic Tb$_3$Si$_2$Ge$_2$ phase into a zero magnetic field, into the small-volume orthorhombic Tb$_3$Si$_2$Ge$_2$, which is stable in a zero magnetic field below $T_C$. In order to verify the sequence of crystallographic transformations, x-ray powder diffraction measurements were carried out as a function of temperature in constant magnetic fields of 0, 20, and 35 kOe, and as a function of magnetic field at constant temperatures in the close proximity of $T_C$.

The intensity contour map of the x-ray powder diffraction patterns of Tb$_3$Si$_2$Ge$_2$, which were collected in a zero magnetic field during heating from 92 K to 120 K, is shown in Fig. 3. Remarkable differences in the positions and intensities of Bragg peaks between the low-temperature and high-temperature patterns indicate that a structural phase transition occurs between ~102 and 112 K. The low-temperature patterns can be mainly indexed as the orthorhombic, space group $Pnma$, Gd$_3$Si$_2$Ge$_2$-type structure [called the O(1) phase hereafter], while the high-temperature patterns belong to the monoclinic, space group $P112_1/a$, Gd$_3$Si$_2$Ge$_2$-type structure (henceforth, the $M$ phase). The O(1) to $M$ phase transformation is accompanied by discontinuous changes of the lattice parameters and unit cell volumes, which are $\Delta a/a = 1\%$, $\Delta b/b = 0.081\%$, $\Delta c/c = -0.16\%$, and $\Delta V/V = 0.74\%$. The structural transition proceeds via shear displacements of the adjacent layers along the $a$ axis in opposite directions by $\sim 0.2$ Å. Along the $b$ axis, every other interlayer Si(Ge)-Si(Ge) interatomic distance expands by 22.8%—from 2.81(1) Å at 70 K in the O(1) phase to 3.45(3) Å at 110 K in the $M$ phase—while the rest remain unchanged, including the layers themselves. These crystallographic changes are similar to those observed in Gd$_3$Si$_2$Ge$_2$ (Ref. 10) and Tb$_3$Si$_2$Ge$_2$. According to the Rietveld refinement there is a tendency toward partial ordering of Si and Ge atoms. The

![Graph showing phase transitions and phase molar percentage](image)

FIG. 4. (Color online) The concentration of the O(1) phase as a function of temperature determined from Rietveld refinement of the patterns collected during heating and cooling of the zero-field-cooled Tb$_3$Si$_2$Ge$_2$ sample in zero (circles) and 35 kOe (triangles) magnetic fields. The arrows indicate the directions of temperature change. $T_C$ is the onset of the crystallographic phase transition upon cooling in a zero magnetic field. The inset illustrates the magnetization isothersms measured at selected temperatures upon field increasing from 0 to 40 kOe using the same Tb$_3$Si$_2$Ge$_2$ powder that was employed in the x-ray experiment. The magnetization was corrected for demagnetizing and replotted as $M^2$ vs $H/M$ (Arrott plots). $T_C$ is the Curie temperature determined from the Arrott plots.

It is worth mentioning that although the transition from the O(1) to $M$ phase on heating is nearly complete, the inverse transition on cooling, i.e., from $M$ to O(1), is incomplete. Even well below 100 K, 10–15% of the $M$-Tb$_3$Si$_2$Ge$_2$ phase always exists. A similar phenomenon was also reported in the m-situ x-ray powder diffraction studies of Gd$_3$Ge$_4$, with ~6.5% of the high-temperature phase retained at low temperatures, which was explained by existence of microstructure imperfection, such as impurities and defects.

The temperature dependencies of the molar concentrations of the O(1) Tb$_3$Si$_2$Ge$_2$ phase derived from the Rietveld refinement of the x-ray patterns collected in zero and 35 kOe magnetic fields are shown in Fig. 4. Upon cooling in a zero field, the $M$ to O(1) phase transition begins at $T_M = 108$ K, which is close to the Curie temperature (110 ± 1 K) determined from Arrott plots (inset of Fig. 4) for the same sample. The closeness of the zero-field $T_M$ and $T_C$ confirms that the extent of the decoupling of the magnetic and crystallographic phase transitions in Tb$_3$(Si,Ge)$_2$ alloys is composition dependent. We note here that the difference of the $T_C$'s of the powder (~110 K) and the single-crystal (~118 K, Fig. 1) samples used in this study is intrinsic, originating from a strong magneto-crystalline anisotropy (see below), as well as extrinsic, likely enhanced by small compositional differences of two different batches of samples.
which has been observed in both the tri-arc and Bridgman-grown crystals.\textsuperscript{25,26}

Figure 4 also shows that the magnetic field shifts the crystallographic phase transformation to higher temperatures and makes it less sharp, indicating that the magnetic field has a strong effect on the crystal structure change in Tb$_5$Si$_2$Ge$_{18}$ near the $T_C$, i.e., a strong magnetoelastic effect is involved. The linear relationships between the onset temperatures of the $M$ to $O(1)$ crystallographic phase transitions ($T_{O(1)}$) and the magnetic field are illustrated in Fig. 5. The slope, $\Delta H/\Delta T_{O(1)}=2.9\pm0.2$ kOe/K, is nearly the same as the average value of the rate of increase of the critical magnetic field with temperature for the PM to FM metamagnetic-like transitions with the field along the $a$ axis (2.64±0.02 kOe/K). However, along the $b$ axis there is no metamagnetic-like transition at fields less than 70 kOe; and for the $c$ axis, the value of the slope is about twice as large (5.4±0.3 kOe/K). This implies a close relationship between the structural and magnetic phase transitions in Tb$_5$Si$_2$Ge$_{18}$, which is further supported by the results of the rotational in situ x-ray powder diffraction experiments, as shown in Fig. 6.

The magnetic field dependencies of the molar concentration of the $O(1)$ phase determined from the x-ray powder diffraction and the bulk magnetization of the single Tb$_5$Si$_2$Ge$_{18}$ powder sample measured at the same constant temperature 112 K (2 K above $T_C$) indicate that both the crystallographic and magnetic phase transformations induced by field remain incomplete (Fig. 6). A zero to 40 kOe magnetic field increase causes an increase of 8.8% to 36.6% of the $O(1)$ phase content, and this trend is consistent with the change of the magnetization, which varies from ~20% to 55% of the technical saturation value, assuming that the initial behavior in fields below ~10 kOe is due to domain rotation of the ferromagnetically ordered $O(1)$, and possibly $M$-Tb$_5$Si$_2$Ge$_{18}$. The existence of a broad metamagnetic-like transition in the Tb$_5$Si$_2$Ge$_{18}$ powder is seen in the $M(H)$ behavior between ~10 and 25 kOe. The incompleteness of this magnetic transition is evident from the magnetization of the powder at $T=112$ K (2 K above $T_C$) and $H=50$ kOe (only ~120 emu/g), which is far less than the ~204 emu/g value obtained in the magnetization of the single-crystal Tb$_5$Si$_2$Ge$_{18}$ after completing a metamagnetic-like transition under similar conditions ($T=119$ K, 1 K above $T_C$, and $H=40$ kOe) with the field parallel to the $a$ axis. We believe that the incompleteness of the magnetic phase transition in the powder is associated with the magnetocrystalline anisotropy of Tb$_5$Si$_2$Ge$_{18}$. A 40 kOe magnetic field can only induce the metamagnetic-like transitions in the grains with their $a$-axis directions parallel or nearly parallel to the applied field. Assuming complete randomness in the powder sample, about 1/3 of the grains will be close to fulfilling this constraint and undergo the transition, which matches the observed changes in the crystallography and magnetism fairly well. This correlation of the degrees of incompleteness of crystallographic and magnetic phase transitions once again indicates an intimate relationship between the crystaline and magnetic susceptibilities, supporting the notion that the magnetocrystalline anisotropy results in some complications, such as making the field-induced structural transition in Tb$_5$Si$_2$Ge$_{18}$ dependent on the direction of the field, the atomic scale mechanism, i.e., the field-induced displacements of the atomic layers along the $a$ axis, remains identical for both the Tb$_5$Si$_2$Ge$_{18}$ and Gd$_5$(Si$_{18-x}$Ge$_x$)$_3$ systems.

Since the crystal structure change brings an additional contribution from the lattice during the transition, the magnetocaloric effect of a material exhibiting a magnetostuctural transition is usually much stronger than that of a conventional ferromagnet with only a magnetic contribution.\textsuperscript{8} Thus, it is reasonable to expect greater values of the magnetocaloric effect when magnetic field is applied parallel to the
FIG. 7. (Color online) The magnetocaloric effect ($-\Delta S_M$) as a function of temperature for the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ single crystal, with $\mathbf{H}||\mathbf{a}$, $\mathbf{H}||\mathbf{b}$, and $\mathbf{H}||\mathbf{c}$, calculated from the magnetization isotherms for a change in the magnetic field from 0 to 50 kOe.

$a$ and $c$ axes than when the field is parallel to the $b$ axis in Tb$_3$Si$_2$Ge$_2$. The magnetocaloric effect, $-\Delta S_M$, was evaluated from the $M(H)$ data according to the Maxwell relation $(\delta S_M/\delta H)_{T} = (\delta M/\delta T)_{H}$, and the results are displayed in Fig. 7. As expected, the maximum values of the $|\Delta S_M|$ with field along the $a$ and $c$ axes (40$\pm$2 and 38$\pm$2 J/kg K, respectively, for $\Delta H=50$ kOe) are much greater than the values obtained with field parallel to the $b$ axis (35$\pm$2 J/kg K) or the polycrystalline Tb$_3$Si$_2$Ge$_2$ (13.4 J/kg K) under the same conditions. Since the temperature dependencies of the critical fields are different for the field parallel to the $a$ and the $c$ axes (Figs. 1, 2, and 5), accordingly, the $-\Delta S_M(T)$ curves are also quite different.

The magnetocaloric effect of the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ powder is 26$\pm$1 J/kg K for $\Delta H=50$ kOe, which is close to the average value, 27 J/kg K, over the three main crystallographic directions of the single crystal under the same conditions. The $|\Delta S_M|$ of the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ powder is also much smaller that of its counterpart in the Gd$_3$(Si$_2$Ge$_2$)$_3$ family, Gd$_3$Si$_2$Ge$_2$, in which $|\Delta S_M|$ is 62 J/kg K for $\Delta H=50$ kOe at $T_c=140$ K. This is understandable because the magnetocrystalline anisotropy of the Gd-containing compound is much smaller than that of the Tb-containing material. Additional reduction of the magnetocaloric effect in the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ compound compared to Gd$_3$Si$_2$Ge$_2$ is related to the differences in the completeness of the structural transitions and in the non-negligible crystalline electric field effects present in the Tb-containing compound. We note that the $|\Delta S_M|$ of the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ powder is about twice that of the polycrystalline Tb$_3$Si$_2$Ge$_2$ (13.4 J/kg K for $\Delta H=50$ kOe). Given that the magnetic and structural transitions in Tb$_3$Si$_2$Ge$_2$ are decoupled, the enhancement of the magnetocaloric effect in the Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ powder may be explained by the magnetic-field-induced crystalline phase transition overlapping with the ferromagnetic ordering. This conclusion finds further support in the fact that when both transitions in Tb$_3$Si$_2$Ge$_2$ are recoupled by hydrostatic pressure, $|\Delta S_M|$ here reaches $\sim$22.1 J/kg K, which is close to that observed in Tb$_3$Si$_2$Ge$_2$ at atmospheric pressure.

Overall, the magnetocaloric effect of Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ exhibits an extremely strong anisotropy (Fig. 7), which directly correlates with the differences in the magnetic hardness along the three principal crystallographic directions; the easier it is to fully magnetize the material, the stronger is the magnetocaloric effect. As far as we are aware, such an extreme anisotropy of the magnetocaloric effect has not been observed among the members of the $R_3$(Si$_2$Ge$_2$)$_3$ family nor among other materials for which the anisotropy of the magnetocaloric effect has been studied.

The anisotropic behavior of the metamagnetic-like transition and magnetocaloric effect in Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ can be understood from the magnetocrystalline anisotropy originating from crystalline electric field interactions, as has been reported in other rare-earth intermetallic compounds with distinctly anisotropic crystal lattices and nonspatial 4$f$ electron wave functions of the lanthanide. The persistence of the magnetocrystalline anisotropy in the paramagnetic state of Tb$_3$Si$_2$Ge$_2$Ge$_{1.8}$ is seen in the temperature dependencies of the inverse magnetic susceptibility along the three main crystallographic directions in Fig. 8. The paramagnetic Weiss temperature ($\Theta_W$) was derived from a least-squares fit of the experimental data to the Curie-Weiss law over the temperature range of 200–300 K for the magnetic field parallel to the $a$, $b$, and $c$ axes. The respective $\Theta_W$'s are 117.3(1), 80.93(4), and 105.8(1) K, and the corresponding effective magnetic moments ($\mu_{eff}$'s) are 10.152(2), 10.047(1), and 10.091(1) $\mu_B$ per Tb atom, where the numbers in parentheses represent the uncertainties in the last significant digits determined from the corresponding least-squares standard deviations. The moments are slightly larger than the theoretical value $g_J(J+1)=9.72 \mu_B$, which is probably due to non-negligible contribution from 5$d$ conduction electrons, observed in many $RM_T$ compounds and the pure metals themselves. Among the three principal crystallographic directions, the values of the $\Theta_W$'s and $\mu_{eff}$'s for the magnetic field along the $a$ axis are the greatest, and those for the $b$ axis are the smallest, indicating that the $a$ axis remains the mag-
netic easy axis and the b axis is the hard direction in the paramagnetic state. Since the alignment of the magnetic moments with the field induces a strain that should be proportional to the magnetization in the paramagnetic state, the resultant stress under the same magnitude of the magnetic field along the a axis would be greater than that for the c and b axes, thus explaining the lower critical magnetic fields along the a axis. A sufficient field-induced stress, in turn, induces the monoclinic to orthorhombic crystallographic transition above the zero magnetic field \( T_c \). Similar to \( \text{Gd}_2\text{Si}_2\text{Ge}_2 \), the two \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) phases are expected to have different temperature dependencies of the magnetization,\(^{29}\) and the observed anisotropic magnetization behavior (Figs. 1 and 2) resembles anisotropic metamagnetic-like transitions.

The coupling of the magnetic and crystallographic phase transitions by applying a magnetic field at temperatures greater than \( T_c \) in \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) echoes the similar coupling induced by a hydrostatic pressure in \( \text{Gd}_2\text{Si}_2\text{Ge}_2 \).\(^{30}\) This behavior is different from that observed in \( \text{Gd}_2\text{Si}_2\text{Ge}_2 \), where the crystallographic and magnetic phase transitions between the two polytypes remain coupled for any magnetic field less than 100 kOe, or any pressure between 1 bar and 9 kbar over a composition range of 0 ≤ \( x \) ≤ 0.5. For \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{2} \) under ambient pressure, the decoupling of the magnetic and structural transitions is ~10 K,\(^{19}\) which is larger than 5 K or less observed in \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \). Furthermore, magnetic fields under 120 kOe could not induce the metamagnetic-like transition above \( T_c \).\(^{10}\) Thus, unlike \( \text{Gd}_2\text{Si}_2\text{Ge}_2 \), the coupling/uncoupling of the magnetic and structural transformations is composition, magnetic field, and pressure dependent in \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \). This difference in the behaviors of these two closely related systems should be attributed to the single-ion anisotropy of Tb, which in addition to indirect exchange interactions that are dominant in both systems, introduces a non-negligible magnetoelastic component in the Tb-based materials.

**CONCLUSIONS**

First-order, magnetic-field-induced, metamagnetic-like transitions were observed in the single-crystal \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) with the field parallel to the a and c axes, but not for the b axis. Consequently, the giant magnetocaloric effect has been observed when the field is parallel to the a and c axes. *In situ* x-ray powder diffraction measurements of \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) showed that the crystallographic phase transformation between the \( O(1) \) and \( M \) phases is strongly influenced by the applied magnetic field, indicating the strong magnetoelastic coupling.

Applying a magnetic field less than 40 kOe isothermally just above the \( T_c \) of a powder sample of \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) cannot drive either the crystallographic or the magnetic phase transformation to completion, and the \( O(1) \) phase concentration changes concurrently with the bulk magnetization of the \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) powder subjected to an applied magnetic field. These observations indicate that the metamagnetic-like transition above \( T_c \) in \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) is of magnetoelastic origin, and the magnetic and structural phase transitions become coupled in magnetic field greater than ~10 K Oe applied a few Kelvin above the zero magnetic field \( T_c \). The magnetocrystalline anisotropy plays an important role in these transitions and accounts for the unusual features found in the \( \text{TB}_{5}\text{Si}_{12}\text{Ge}_{18} \) material.

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Spontaneous generation of voltage in single-crystal Gd$_2$Si$_2$Ge$_2$

during magnetostructural phase transformations

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The spontaneous generation of voltage (SGV) in single-crystal and polycrystalline Gd$_2$Si$_2$Ge$_2$ during the coupled magnetostructural transformation has been examined. Our experiments show reversible, measurable, and repeatable SGV responses of the materials to the temperature and magnetic field. The parameters of the response and the magnitude of the signal are anisotropic and rate dependent. The magnitude of the SGV signal and the critical temperatures and critical magnetic fields at which the SGV occurs vary with the rate of temperature and magnetic-field changes. © 2006 American Institute of Physics. [DOI: 10.1063/1.2162027]

Since their rediscovery in 1997,1,2 the R$_2$(Si$_2$Ge$_{2n-1}$)$_2$, where $R$ is a lanthanide metal, continue to attract considerable attention. This is because of their interesting physical properties, such as the giant magnetocaloric effect,1,3-4 colossal magnetostriction,5-8 giant magnetoresistance,9-16 and spontaneous generation of voltage (SGV),17 that have been observed during the first-order magnetostructural, ferromagnetic-orthorhombic to paramagnetic-monoclinic (on heating), phase transformation (see Refs. 5,18). Among them, the SGV is especially intriguing because it may result in the development of sensors, which can respond not only to changes in temperature, pressure, and/or magnetic field but most importantly to the rates of their changes without the need for a complicated analysis of signals. Furthermore, all of this can be done by a single sensor requiring no standby power.

The SGV in the R$_2$(Si$_2$Ge$_{2n-1}$)$_2$ system was reported by Levin et al. in several polycrystalline samples of Gd$_2$(Si$_2$Ge$_{2n-2}$)$_2$.17 Because a current was not supplied, the voltages observed across the samples were regarded as spontaneous. The SGV occurs near first-order magnetostructural phase transformations. Here we report on the SGV during the first-order phase transition in several single-crystal Gd$_2$Si$_2$Ge$_2$ samples. In addition to the SGV behavior as a function of temperature and magnetic field, we also examine the anisotropy of the signal and its dependence on the variable rates of change of these stimuli.

The Gd$_2$Si$_2$Ge$_2$ single crystal was prepared using the Bridgman method.19 Three parallelepiped-shaped samples were cut from a large grain by wire electric discharge machining. The longest side of each sample was parallel to one of the three major crystallographic directions [100], [010], or [001], and specimen dimensions were $3.66 \times 1.82 \times 0.49$, $4.06 \times 1.03 \times 1.00$, and $5.6 \times 2.0 \times 0.92$ mm$^3$, respectively. The SGV behaviors of a polycrystalline Gd$_2$Si$_2$Ge$_2$ sample with the dimensions of $6.57 \times 2.48 \times 1.85$ mm$^3$ were also measured in order to verify previous observations17 and to compare them with the single-crystal samples.

The dc voltages across the samples were measured by a standard two-probe method and recorded as functions of time by a Keithley 181 nanovoltmeter. Readouts from the nanovoltmeter were computer recorded every 0.25 s. The temperature and magnetic-field changes exerted on the samples were regulated by a LakeShore Model 7225 magnetometer. The samples were subjected to the temperature and magnetic-field variations above and below their zero-field transition temperatures, at rates $-7$ to $+3$ K/min and $-70$ to $+70$ kOe/min. The magnetic fields were applied and the voltages were measured along the longest side of each sample. The misorientation between the directions of the magnetic-field vector and the crystal axes were less than $\pm 5^\circ$. The SGV signal background caused by a minor thermal noise and drift of the nanovoltmeter were automatically subtracted before recording every sequence. The temperature readings from the sensor may deviate from the actual sample temperature by $\pm 2$ K due to the design of the magnetometer.

The resolution of the Keithley 181 nanovoltmeter is 100 nV. The dc magnetization was measured using the same magnetometer.

The SGV signals of a Gd$_2$Si$_2$Ge$_2$ single-crystal sample along the [010] direction as functions of temperature and the rate of temperature change in a zero magnetic field are displayed in Fig. 1. The characteristics of the temperature-induced SGV signals are similar for all three samples. The onsets temperatures of the SGV signals are located within 2 K of the Curie temperature ($T_C$) which are 269 and 259 K for warming and cooling, respectively, confirming that the origin

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of the SGV is the coupled magnetic and crystallographic phase transformation. A thermal hysteresis of about 10 K of the SGV signals is observed. All signals are S shaped, starting at Tc and ending at temperatures 2–4 K higher or lower than Tc upon heating or cooling, respectively. A higher-temperature sweep rate increases the magnitude of the SGV signal and raises or lowers the temperature at which the SGV signal appears upon heating or cooling, respectively. The shapes of the SGV signals are quite similar to the thermal emf signals observed during the freezing of water, the melting of tin, and the solidification of CuBr, suggesting that a similar mechanism may be responsible for these signals.20

Figure 2 shows the isothermal SGV signals induced by sweeping the magnetic field at a rate of ~40 kOe/min in the single-crystal samples along three principal crystallographic directions and in a polycrystalline sample. The isothermal dc magnetization data measured at the same temperatures are also shown in Fig. 2. Because there are compositional differences in different single-crystal samples (see Ref. 16 for details), the temperatures were normalized to the individual Tc's determined for each specimen from low-field dc magnetization. The onsets and offsets of the SGV signals triggered by magnetic fields coincide, respectively, with the rapid increase of the magnetization and its saturation due to the magnetic-field-induced phase transitions between the paramagnetic and ferromagnetic states. Upon field increasing, the SGV signal starts at the onset of the paramagnetic-monoclinic (PM) to ferromagnetic-orthorhombic (FM) transition, reaches a maximum and then drops to a minimum, and finally goes back to zero when the magnetic transition is complete. Upon field decreasing, the shape of the SGV signals does not change much, with a maximum appearing first, followed by a minimum. The onset and end points of the SGV signals occur at lower fields during demagnetizing than during magnetizing, which is normal for a first-order phase transformation. The magnetic fields of the onsets and especially of the ends of the SGV signals are slightly different for different crystallographic directions, demonstrating weak anisotropy.

The shapes of the SGV signals are similar for the [010] and [001] direction samples when subjected to a same variation of a same trigger (temperature or magnetic field), while the shape of the [100] direction sample seems unique. As it is known from the structural characterization of the Gd₃Sb₂Ge₅, the shear movement of the slabs during the coupled magnetostriuctive phase transformation occurs along the [100] direction,12 and this is likely the reason for the uniqueness of the SGV behavior of the [100] direction sample. There is a small difference in the magnitudes of the SGV signals for the single-crystal samples along different crystallographic directions. Since the magnitude of the SGV signal depends on the sample shape and the distance between the two electrical connections to the sample, we believe that this small difference in the magnitudes is extrinsic. The magnitudes of the SGV signals for the polycrystalline sample, however, are about three times smaller than those of the single-crystal samples despite similar shapes and locations of the electrical connections to the samples. Thus, a smaller SGV signal in polycrystal is intrinsic. This feature correlates well with the fact that the first-order transitions in single-crystal samples are usually sharper than those in polycrystalline samples of the same composition, and it is in line with the results from the magnetic force microscopy and thermal expansion studies of a Gd₃Sb₂Ge₅ single crystal.21

As mentioned above, the higher-temperature sweep rate increases the magnitude of the SGV signal. For the magnetic-field-induced SGV signals, the increase of the rate of change of the stimulus also increases the magnitude of the signal, as shown in Fig. 3(a). The critical field at which the SGV signal starts also exhibits a systematic change with changing the magnetic-field sweep rate. As shown in Fig. 3(b), the increased field sweep rate shifts the critical field to lower values for all the samples. This is in line with an earlier observation that the critical field of the magnetostriuctive transition in Gd₃Ge₅ is also field sweep rate.
There are some differences in the absolute values of the magnitudes of the signals and the values of the $\Delta H_C = H_C - H_C^*$, where $H_C$ is the critical magnetic field at 1 kOe/min for different samples, but we believe that they may be extrinsic for different single-crystal samples. The difference between the polycrystalline and single-crystal samples is intrinsic due to the reasons mentioned above.

The main reason for the SAGV was sought to be the Seebeck effect, given the similarity of the SAGV profile and the signal recorded from a differential thermocouple simultaneously. A compositional difference and a temperature difference on the two ends of the sample triggers the phase transformation from one specific end, propagating to another. The heat release or absorption during this process gives rise to the S shape and polarity change of the SAGV signal when the direction of temperature or and magnetic-field change is reversed. It is worth noting, however, that when a sample is flipped without reversing the polarity of the electrical connections, the polarity of the SAGV signal also reverses. This behavior supports the notion that there is a small gradient of composition along the sample, and therefore a slight change of the $T_C$, because a temperature gradient caused by the instrument should always be the same, regardless of how the sample is mounted.

In summary, the spontaneous generation of voltage in both single-crystal and polycrystalline Gd$_2$Si$_2$Ge$_2$ samples has been studied as a function of temperature, magnetic field, and rates of their changes. The critical temperatures and magnetic fields at which the SAGV signals appear nearly coincide with the Curie temperatures and the critical magnetic fields at which the first-order magnetostructural phase transformations occur. This observation confirms the intimate relationship between the SAGV and the coupled magnetic crystallographic phase transformation. A weak anisotropy was observed in single-crystal Gd$_2$Si$_2$Ge$_2$ samples through their different SAGV responses. The magnitude of the SAGV signal clearly increases with the rate of the temperature and magnetic-field change. The rate of stimuli changes also shifts the critical temperatures and critical magnetic fields. Although more research is needed to better map out the details of the SAGV behavior in the Gd$_2$Si$_2$Ge$_2$ alloy, it is a likely candidate for a smart temperature and magnetic-field sensor material for near-room-temperature applications, adding another aspect of its potential manifold applications.

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Spontaneous generation of voltage in the magnetocaloric compound Tb$_5$Si$_2$Ge$_{1.8}$ and elemental Gd

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1. Introduction

Interesting physical properties, such as the giant magnetocaloric effect (GMCE), giant magnetoresistance (GMR), colossal magnetoresistance, and spontaneous generation of voltage (SGV) [1-3] are known to occur in rare earth intermetallic compounds $R$($R'$)$_2$Ge$_x$, where $R$ is a lanthanide element. All of these effects originate from first-order coupled magnetic and crystallographic phase transformations when $R$ = Gd [1]. When $0 < x < 0.3$, the phase transformation is between a ferromagnetic orthorhombic phase [011]/[FM] and a different orthorhombic phase in its antiferromagnetic state [011]/AFM. When $0.4 < x < 0.5$, the transformation is between a ferromagnetic orthorhombic phase [011]/FM and a paramagnetic monoclinic phase [M]/PM. Temperature, magnetic field, and/or pressure have been identified as triggers of these transformations [1,4].

Different from Gd$_5$(Si$_2$Ge$_x$)$_3$, the magnetic and crystallographic phase transformations of Tb$_5$(Si$_2$Ge$_x$)$_3$ between [011]/FM and [M]/PM are decoupled by $-10$ K and less than 5 K when $x = 0.5$ and 0.55, respectively [5-7]. These independent magnetic and crystallographic phase transformations can be decoupled by applying moderate hydrostatic pressures and/or magnetic fields as has been demonstrated for a polycrystalline sample with $x = 0.5$ and a single crystal with $x = 0.55$ [6,8]. The decoupling results in a 40% enhancement of the GMCE in polycrystalline Tb$_5$Si$_2$Ge$_{1.6}$ [8]. It is worth noting that in a single crystal of Tb$_5$Si$_2$Ge$_{1.6}$ ($x = 0.55$), the GMCE only occurs when the magnetic field is applied parallel to the $a$- and $c$-axes [8]. Interplay between decoupling and decoupling of the magnetic and structural transformations indicates a complex energy landscape separating different magnetic and crystallographic phases, and the complexity is enhanced by the single ion anisotropy of Tb$^{3+}$ when compared to Tb$^{3+}$ [6].

The SGV has been observed in both polycrystalline and single crystalline Gd$_5$(Si$_2$Ge$_x$)$_3$ in the vicinity of the Curie temperature ($T_c$) when either temperature was varied at constant field or when magnetic field was changed isothermally [2,3]. The origin of SGV in these compounds is believed to be thermoelectric effect, i.e., Seebeck effect [2,3]. Because a small compositional difference is always present between the two ends of a sample and because small temperature gradients are always present across a sample whose temperature is actively controlled, phase transformation typically starts at one end of the specimen and then propagates to the other. The heat release or absorption during this process gives rise to measurable temperature gradients necessary for the generation of the thermoelectric signal.

The study of SGV in Tb$_5$(Si$_2$Ge$_x$)$_3$ compounds is a continuation of previous studies of Gd$_5$(Si$_2$Ge$_x$)$_3$ [2,3]. To gain a better understanding of the role that different factors play in the appearance of the SGV, a single crystal of Gd metal has also been examined with respect to both temperature and magnetic field-induced spontaneous voltage. Among the materials undergoing second order magnetic order–disorder transformations, elemental Gd has one
of the highest MCE's around room temperature, which is about half that observed in GdSi₂SiGe₁₂ [9]. A small anisotropy due to dipolar and spin-orbit couplings results in the c-axis of Gd being the magnetic easy axis immediately below $T_C \approx 289$ K [10,11].

2. Experimental

Two GdSi₂SiGe₁₂ single crystals were grown by the tri-arc method [12] from high purity Th, Si, and Ge mixed in the approximate stoichiometry. The two Th stocks [95.67 at. % (90.97 wt. %) and 99.89 at. % (99.99 wt. %) pure with respect to all other elements in the periodic table] were prepared by the Materials Preparation Center (MPC) of the Ames Laboratory [13]. The Si and Ge were purchased from commercial vendors, and were better than 99.99 wt. % pure. The as-grown crystals were oriented using backscatter Laue X-ray diffraction.

Three rectangular parallelepiped samples were cut by spark erosion. They were 5.01 mm × 0.08 mm × 0.44 mm, 3.38 mm × 0.04 mm × 0.57 mm, and 4.66 mm × 0.22 mm × 0.67 mm with the longest dimension of each along the a-, b-, and c-axes, respectively. The a- and b-axes samples came from the single crystal prepared using 99.67 at. % pure Th metal, and the c-axis sample came from the 99.89 at. % pure Th. Four thin platinum wires were attached to each sample with H2ES Epoxi silver epoxy manufactured by Epoxy Technology. The samples were also used for an electrical resistivity study, results of which will be published elsewhere. The distance between the voltage contacts was 1.20, 1.34, and 3.00 mm for the a-, b-, and c-axes samples, respectively. Typical contact resistances of the freshly prepared samples were between 1 and 75Ω.

The single crystal Gd was prepared using the strain-anneal method from polycrystalline Gd metal and a strain anneal also prepared by the MPC. The metal was 99.999 at. % (99.999 wt. %) pure with respect to all other elements in the periodic table. A rectangular parallelepiped sample was cut using the spark erosion technique from a large grain. Its dimensions were 9.12 mm × 1.02 mm × 1.11 mm with the longest side along the c-axis. Four thin platinum wires were attached to the sample by using a spot welding technique. The distance between the voltage contacts was 750 μm. Contact resistances of the freshly prepared samples were below 1Ω. The SGV measuring method, instrument set-up, and experimental errors were described elsewhere [3].

3. Results and discussion

As shown in Fig. 1, temperature induced SGV appears along all three major crystal axes of GdSi₂SiGe₁₂ between 110 and 118 K, where the crystallographic and magnetic phase transformations occur [6,7]. The SGV starting temperatures are different upon heating and cooling by $\approx$ 5 K. This separation is nearly the same as the extent of thermal hysteresis of the crystallographic phase transformation [6]. Therefore, one can associate the SGV with the crystallographic transformation, and the SGV also shows that the SGV increases with the increased rate of temperature change, which is similar to that observed in GdSi₂Ge₁₂ [3]. On the other hand, a magnetic field of 40 kOe and lower can trigger the SGV only when the field vector is parallel to the a-axis. A representative result at 120 K is displayed in Fig. 2. This observation is different from GdSi₂Ge₁₂, where the SGV occurs when a magnetic field is not thermally applied along any of the three major crystallographic directions in the vicinity of $T_C$ [3].

Both neutron and X-ray powder diffraction studies of GdSi₂SiGe₁₂ illustrate a temperature-induced first-order crystallographic phase transformation involving a large unit-cell volume change of $\approx$ 1% [6,7]. By rearranging the Clausius-Clapeyron equation [14] \[ \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta (\Delta V)}{\Delta T(dP/dT)\Delta V} \], where $P$, $T$, $S$, $V$, and $E$ are the pressure, temperature, entropy, volume, and enthalpy, respectively, it is obvious that the enthalpy change,
for the temperature gradients necessary for the observation of the field-induced SGV.

The roles played by latent heat and MCE in SGV were further studied by using a single crystal of Gd metal. No SGV occurs in the vicinity of $T_c = 293$ K as long as the magnetic field remains constant.

Since the phase transition at $T_c$ is a pure second-order magnetic one, no latent heat is involved here. The absence of SGV in the elemental Gd near $T_c$ supports the notion that the temperature-induced SGV depends on the latent heat of the first-order phase transformation.

The SGV in Gd can be triggered by applying a magnetic field isothermally in the vicinity of $T_c$. Fig. 3 exhibits the SGV of Gd as a function of magnetic field applied along the c-axis between 278 and 304 K with a field increasing at the rate of $-40$ kOe/min. The largest magnitude of SGV, which is taken as the voltage difference between the positive and negative peaks, is $-2$ $\mu$V. It is observed at 294 K, i.e., in the immediate vicinity of the maximum MCE, which occurs at 293 K. This is much smaller than the SGV of GdSi$_2$Ge$_2$ [3] and Tb$_2$Si$_2$Ge$_2$ single crystals (see Fig. 2). Consistent with the behavior of the MCE in Gd, which decreases gradually as the temperature is further and further away from $T_c$, (see Ref. [15]), the magnitude of the SGV signal exhibits a similar reduction with temperature as is clearly seen in Fig. 3. Furthermore, since the thermoelastic signal is proportional to the temperature difference ($\Delta T$) between two ends of a specimen, and GdSi$_2$Ge$_2$ and Tb$_2$Si$_2$Ge$_2$ have a greater MCE compared to that of Gd, one concludes that the MCE determines $\Delta T$, and therefore, determines the magnitude of the magnetic field-induced SGV.

4. Conclusions

Temperature-induced SGV has been observed in Tb$_2$Si$_2$Ge$_2$ along three major crystallographic axes near $T_c$, but not in a Gd single crystal. This suggests that a phase transformation involving a large volume change, i.e., a large latent heat, is necessary for the temperature-induced SGV. The magnetic field-induced SGV has been observed in Tb$_2$Si$_2$Ge$_2$ near $T_c$ only with $H_{||c}$, but not with $H_{||h}$ and $H_{||e}$ when $H = 40$ kOe. The field-induced SGV has also been observed in Gd near $T_c$. These observations indicate that a first-order magnetostructural phase transformation is not a necessary condition for SGV to occur. But a large MCE for the magnetic field-induced SGV is necessary for the latter in order to be observed.

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References