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Crystallography, anisotropic metamagnetism, and magnetocaloric effect in $Tb_5Si_{2.2}Ge_{1.8}$

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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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 magnetocrystalline 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Gd_5(Si_xGe_{1-x})_4$ compounds show a strong magnetocaloric effect when they undergo coupled magnetostructural phase transitions, which is clearly evident from the concurrent change of the magnetization and crystal structure observed in Gd_5Ge_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 $Gd_5(Si_xGe_{1-x})_4$ in the intermediate composition range ($x \cong 0.5$), 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 $Gd_5(Si_xGe_{1-x})_4$ are also referred to as metamagnetic-like transitions.

The $Tb_5(Si_xGe_{1-x})_4$ 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 $Gd_5(Si_xGe_{1-x})_4$ near $x=0.5$. However, unlike in $Gd_5Si_2Ge_2$, no clear metamagnetic-like behavior was observed in the magnetization of polycrystalline $Tb_5Si_2Ge_2$, 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 $R_5(Si_xGe_{1-x})_4$ family, where R is a rare earth element. Interestingly, the magnetic and structural transitions in $Tb_5Si_2Ge_2$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ ($x=0.55$), not only the separation of the magnetic and crystallographic transitions is smaller than the ~10 K reported for $Tb_5Si_2Ge_2$ ($x=0.5$) 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 crystallography in the $Tb_5(Si_xGe_{1-x})_4$ system, and the origin of the large magnetocaloric effect, we have conducted dc magnetization and *in situ* x-ray powder diffraction studies of $Tb_5Si_{2.2}Ge_{1.8}$. 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 $Tb_5Si_{2.2}Ge_{1.8}$ single crystal for the magnetization measurements was grown by the tri-arc method[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.*[21] The Tb was prepared by the Materials Preparation Center[23] and contained the following major impurities (in ppm at.): O, 1900; C, 1100; N, 180; 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 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 $1.50 \times 1.94 \times 0.88\ \mathrm{mm}^3$ 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 ±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 $Tb_5Si_{2.2}Ge_{1.8}$ single crystal that was grown by the Bridgman method.[24] The Tb used in this sample was prepared by the Materials Preparation Center[23] and 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 and Ge were purchased from Meldform 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 ±0.02 K below 50 K and within ±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.

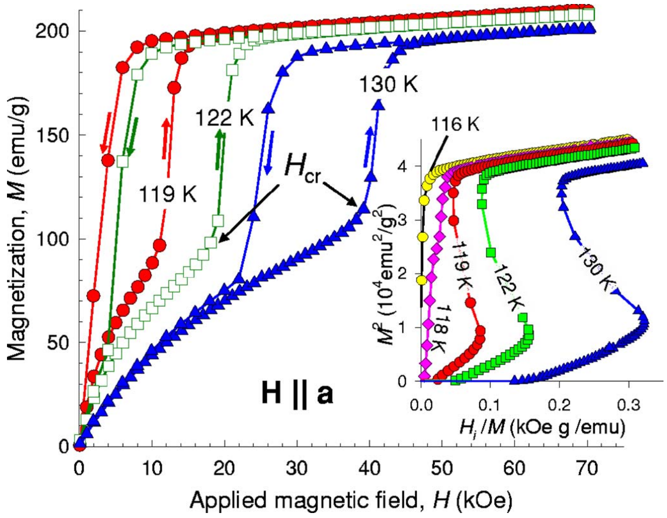

FIG. 1. (Color online) The magnetization isotherms of $Tb_5Si_{2.2}Ge_{1.8}$ single crystal at selected temperatures measured with the applied magnetic field parallel to the a axis. The arrows mark the direction of the field change. The H_{cr}, critical magnetic field, is taken at the onset of the metamagnetic-like transitions upon increasing the field. The inset illustrates the magnetization isotherms measured at selected temperatures with increasing field from 0 to 70 kOe, corrected for the demagnetizing effect, and replotted as M^2 vs H_i/M (Arrott plots).

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[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[27] 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.[28] 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 $T \leqslant 118$ K, the field dependence of the magnetization is that of a typical ferromagnet, in agreement with the microscopic magnetic structure of

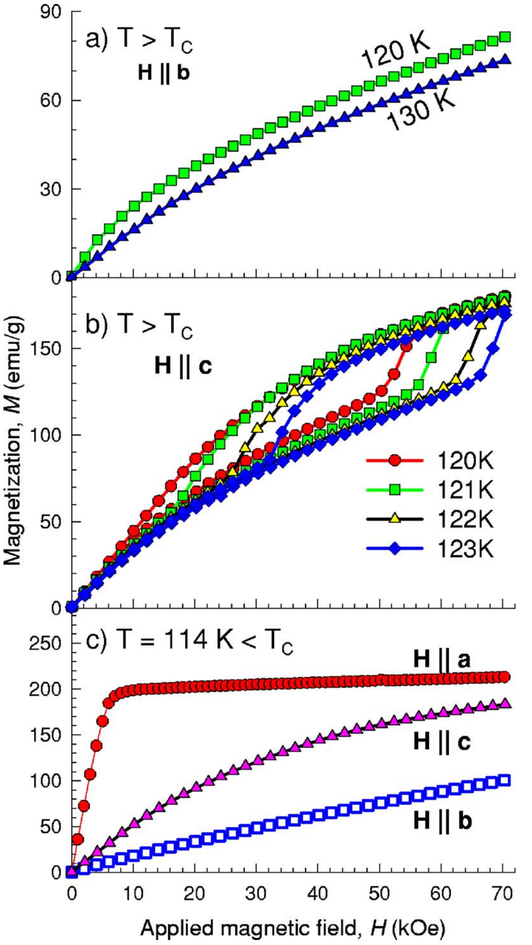

FIG. 2. (Color online) The magnetization isotherms of $Tb_5Si_{2.2}Ge_{1.8}$ single crystal at selected temperatures measured with the applied magnetic field parallel to the *b* axis (a) and *c* axis (b). Panel (c) illustrates three isotherms measured parallel to the three crystallographic axes at the same $T=114$ K, which is ~4 K below $T_C=118$ K.

$Tb_5Si_{2.2}Ge_{1.8}$ 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 μ_B, which is close to the average magnetic moment per Tb atom at 100 K—7.58 μ_B—determined from the neutron scattering study of polycrystalline $Tb_5Si_{2.2}Ge_{1.8}$.[21] These field-induced magnetic transitions are reversible when $T \geqslant 122$ 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 $Gd_5(Si_xGe_{1-x})_4$.[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_{cr} with temperature for the field parallel to the *c* axis (5.4 ± 0.3 kOe/K) is much larger than the same for the field parallel to the *a* axis (2.64 ± 0.02 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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.[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 $Gd_5(Si_xGe_{1-x})_4$ along all three principal crystallographic directions,[16] and they have been regarded as magnetoelastic transformations during which the magnetic and crystal structures change concurrently.[4] According to a recent theoretical study of the electron correlation effects on the magnetostructural transition of $Gd_5Si_2Ge_2$,[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_C^O of the orthorhombic $Gd_5Si_2Ge_2$ being considerably higher than the T_C^M of the monoclinic polymorph. The actual temperature of the magnetostructural transition of $Gd_5Si_2Ge_2$, T_C, is located between T_C^O and T_C^M. 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 $Gd_5Si_2Ge_2$ 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 $Tb_5(Si_xGe_{1-x})_4$ with $x \cong 0.5$ has the same sequence of polymorphs with the same types of crystal structures as $Gd_5Si_2Ge_2$, the metamagnetic-like transitions in $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$. 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,

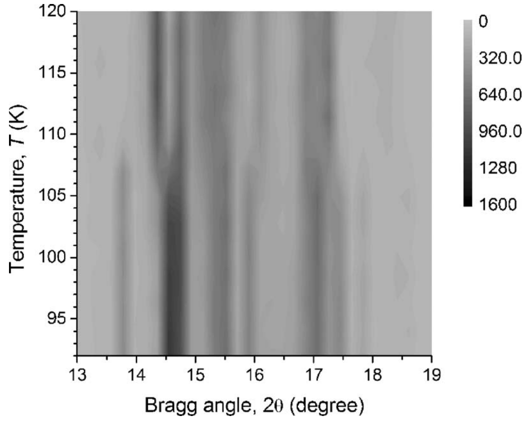

FIG. 3. The intensity contour map of the x-ray powder diffraction patterns of $Tb_5Si_{2.2}Ge_{1.8}$ collected in a zero magnetic field during heating from 92 K to 120 K. All patterns were collected using Mo Kα radiation. Only the range from 13 to 19° 2θ is shown for clarity. The bar on the right represents the intensity scale.

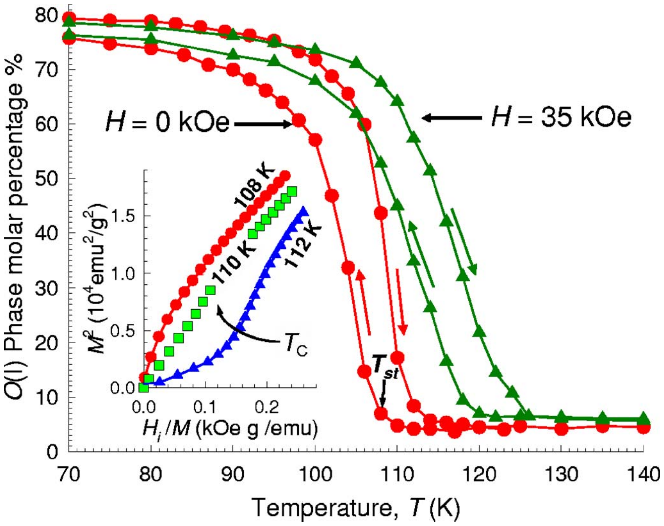

FIG. 4. (Color online) The concentration of the O(I) phase as a function of temperature determined from Rietveld refinement of the patterns collected during heating and cooling of the zero-field-cooled $Tb_5Si_{2.2}Ge_{1.8}$ sample in zero (circles) and 35 kOe (triangles) magnetic fields. The arrows 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 $Tb_5Si_{2.2}Ge_{1.8}$ powder that was employed in the x-ray experiment. The magnetization was corrected for demagnetizing and replotted as M^2 vs H_i/M (Arrott plots). T_C is the Curie temperature determined from the Arrott plots.

but in a single crystal it may be approximated by a uniaxial pressure. Considering the strong dependence of the crystallographic-only transformation in $Tb_5Si_2Ge_2$ on hydrostatic pressure,[20] the increased magnetic field, therefore, should be able to convert some or all of the large-volume monoclinic $Tb_5Si_{2.2}Ge_{1.8}$, which is an equilibrium phase above T_C in a zero magnetic field, into the small-volume orthorhombic $Tb_5Si_{2.2}Ge_{1.8}$, 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.

The intensity contour map of the x-ray powder diffraction patterns of $Tb_5Si_{2.2}Ge_{1.8}$, 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_5Si_4-type structure [called the O(I) phase hereafter], while the high-temperature patterns belong to the monoclinic, space group $P112_1/a$, $Gd_5Si_2Ge_2$-type structure (henceforth, 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 ~0.2 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 $Gd_5Si_2Ge_2$ (Ref. 10) and $Tb_5Si_2Ge_2$.[18] According to the Rietveld refinement there is a tendency toward 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 $Gd_5Si_2Ge_2$.[10]

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, 10–15% of the M-$Tb_5Si_{2.2}Ge_{1.8}$ phase always exists. A similar phenomenon was also reported in the *in-situ* x-ray powder diffraction studies of Gd_5Ge_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.[9]

The temperature dependencies of the molar concentrations of the O(I) $Tb_5Si_{2.2}Ge_{1.8}$ phase derived from the Rietveld refinement of the x-ray patterns collected in zero and 35 kOe magnetic fields are shown in Fig. 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 Fig. 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 $Tb_5(Si_xGe_{1-x})_4$ alloys is composition dependent.[19,21] 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 magnetocrystalline anisotropy (see below), as well as extrinsic, likely enhanced by small compositional differences of two different batches of samples,

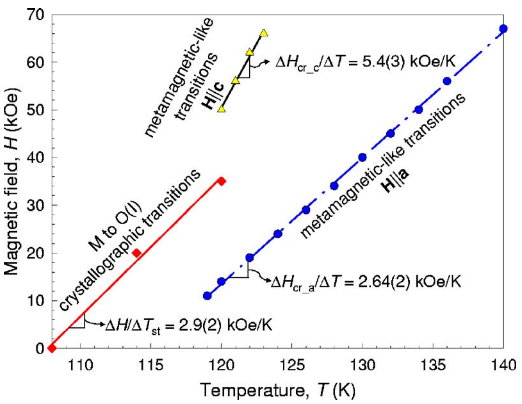

FIG. 5. (Color online) The relationships between the magnetic fields and the onset temperatures of the M to O(I) crystallographic phase transitions (T_{st}'s) for the $Tb_5Si_{2.2}Ge_{1.8}$ powder; and that between the critical magnetic fields (H_{cr}'s) and temperature of the PM to FM metamagnetic-like transitions for $\mathbf{H}\|\mathbf{a}$ and $\mathbf{H}\|\mathbf{c}$ of the $Tb_5Si_{2.2}Ge_{1.8}$ single crystal. The numbers in parentheses represent the uncertainties in the last significant digits determined from the corresponding least-squares standard deviations.

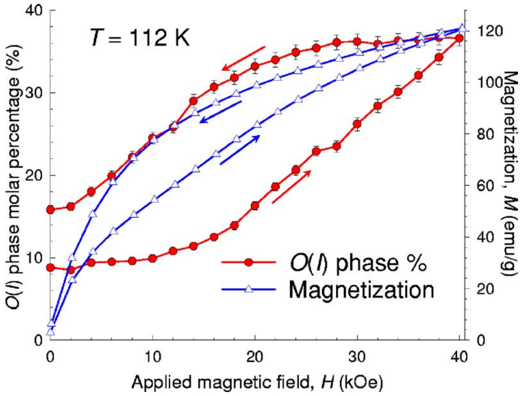

FIG. 6. (Color online) The magnetic field dependencies of the concentration of the O(I) phase (circles, left hand scale) determined from the Rietveld refinement of the x-ray powder diffraction patterns, and the dc magnetization (triangles, right hand scale) of $Tb_5Si_{2.2}Ge_{1.8}$. Both sets of data were measured isothermally after thermal demagnetization of the sample at 230 K and then cooling down to 112 K. The magnetic field was changed in 2 kOe steps between zero and 40 kOe. The arrows indicate the directions of the magnetic field change.

which has been observed in both the tri-arc and Bridgman-grown cyrstals.[22,24]

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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 Fig. 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 $Tb_5Si_{2.2}Ge_{1.8}$, which is further supported by the results of the isothermal *in situ* x-ray powder diffraction experiments, as shown in Fig. 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 (Fig. 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-$Tb_5Si_{2.2}Ge_{1.8}$. The existence of a broad metamagnetic-like transition in the $Tb_5Si_{2.2}Ge_{1.8}$ 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 the ~204 emu/g value obtained in the magnetization of the single-crystal $Tb_5Si_{2.2}Ge_{1.8}$ 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. We believe that the incompleteness of the magnetic phase transition in the powder is associated with the magnetocrystalline anisotropy of $Tb_5Si_{2.2}Ge_{1.8}$. 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 $Tb_5Si_{2.2}Ge_{1.8}$ is a coupled magnetostructural transition, similar to that observed in $Gd_5(Si_xGe_{1-x})_4$.[4,29] Although the magnetocrystalline anisotropy results in some complications, such as making the field-induced structural transition in $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ and $Gd_5(Si_xGe_{1-x})_4$ systems.

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.[8] Thus, it is reasonable to expect greater values of the magnetocaloric effect when magnetic field is applied parallel to the

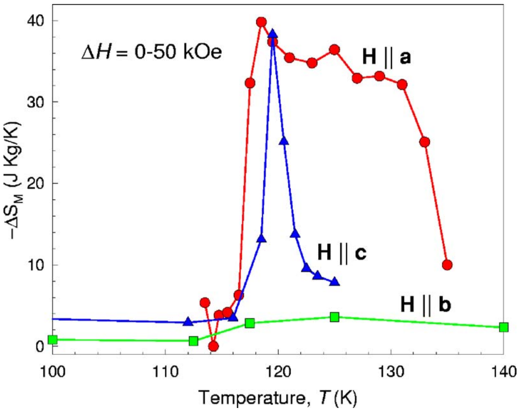

FIG. 7. (Color online) The magnetocaloric effect ($-\Delta S_M$) as a function of temperature for the $Tb_5Si_{2.2}Ge_{1.8}$ single crystal, with $\mathbf{H}\|\mathbf{a}$, $\mathbf{H}\|\mathbf{b}$, and $\mathbf{H}\|\mathbf{c}$, calculated from the magnetization isotherms for a change in the magnetic field from 0 to 50 kOe.

a and *c* axes than when the field is parallel to the *b* axis in $Tb_5Si_{2.2}Ge_{1.8}$. 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 Fig. 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 ΔH=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 polycrystalline $Tb_5Si_2Ge_2$ (13.4 J/kg K)[20] 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 $Tb_5Si_{2.2}Ge_{1.8}$ powder is 26±1 J/kg K for ΔH=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 $Tb_5Si_{2.2}Ge_{1.8}$ powder is also much smaller than that of its counterpart in the $Gd_5(Si_xGe_{1-x})_4$ family, $Gd_5Si_{1.01}Ge_{2.99}$, whose $|\Delta S_M|$ is 62 J/kg K for ΔH=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 $Tb_5Si_{2.2}Ge_{1.8}$ compound compared to $Gd_5Si_{1.01}Ge_{2.99}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ powder is about twice that of the polycrystalline $Tb_5Si_2Ge_2$ (13.4 J/kg K for ΔH =50 kOe).[20] Given that the magnetic and structural transitions in $Tb_5Si_2Ge_2$ are decoupled, the enhancement of the magnetocaloric effect in the $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_2Ge_2$ are recoupled by hydrostatic pressure,[20] $|\Delta S_M|$ here reaches ~22.1 J/kg K, which is close to that observed in $Tb_5Si_{2.2}Ge_{1.8}$ at atmospheric pressure.

Overall, the magnetocaloric effect of $Tb_5Si_{2.2}Ge_{1.8}$ 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 $R_5(Si_xGe_{1-x})_4$ family nor among other materials for which the anisotropy of the magnetocaloric effect has been studied.[30–32]

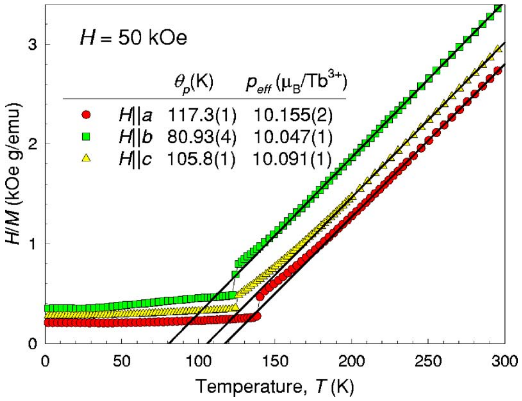

FIG. 8. (Color online) Temperature dependencies of the inverse magnetic susceptibility, H/M, of $Tb_5Si_{2.2}Ge_{1.8}$ measured on heating in a 50 kOe magnetic field parallel to the *a*, *b*, and *c* axes. The lines are linear least-squares fits of the data to the Curie-Weiss law between 200 and 300 K. The inset table gives the paramagnetic Curie temperatures (θ_p's) and effective magnetic moments (p_{eff}'s) derived from these linear least-squares fits, where the numbers in parentheses represent the uncertainties in the last significant digits determined from the corresponding least-squares standard deviations.

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 nonspherical 4*f* electron wave functions of the lanthanide.[33–37] 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 Fig. 8. The paramagnetic Weiss temperatures (θ_p's) were 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 θ_p's are 117.3(1), 80.93(4), and 105.8(1) K, and the corresponding effective magnetic moments (p_{eff}'s) are 10.152(2), 10.047(1), and 10.091(1) μ_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 $g\sqrt{J(J+1)}$=9.72 μ_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 θ_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 $Gd_5Si_2Ge_2$, the two $Tb_5Si_{2.2}Ge_{1.8}$ 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 transformations.

The coupling of the magnetic and crystallographic phase transitions by applying a magnetic field at temperatures greater than T_C in $Tb_5Si_{2.2}Ge_{1.8}$ echoes the similar coupling induced by a hydrostatic pressure in $Tb_5Si_2Ge_2$.[20] This behavior is different from that observed in $Gd_5(Si_xGe_{1-x})_4$, 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 $0 \leqslant x \leqslant 0.5$. For $Tb_5Si_2Ge_2$ 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 $Tb_5Si_{2.2}Ge_{1.8}$. Furthermore, magnetic fields under 120 kOe could not induce the metamagnetic-like transition in $Tb_5Si_2Ge_2$ above T_C.[19] Thus, unlike $Gd_5(Si_xGe_{1-x})_4$, the coupling/uncoupling of the magnetic and structural transformations is composition, magnetic field, and pressure dependent in $Tb_5(Si_xGe_{1-x})_4$. 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.

CONCLUSIONS

First-order, magnetic-field-induced, metamagnetic-like transitions were observed in the single-crystal $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ powder subjected to an applied magnetic field. These observations indicate that the metamagnetic-like transition above T_C in $Tb_5Si_{2.2}Ge_{1.8}$ 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 $Tb_5Si_{2.2}Ge_{1.8}$ material.

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