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Magnetic-martensitic transition of $Tb_5Si_2Ge_2$ studied with neutron powder diffraction

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The effect of the application of an external magnetic field in the paramagnetic phase of the giant magnetocaloric compound $Tb_5Si_2Ge_2$ has been studied by means of macroscopic (magnetostriction and magnetoresistance) and microscopic neutron powder diffraction experiments. As a main result, we have discovered the existence of a ferromagnetic monoclinic phase in these intriguing 5:4 compounds. Long-range ferromagnetism sets in within the monoclinic structure on cooling down before the structural transformation into the orthorhombic phase takes place. Our results may shed some light into understanding the complex coupling between crystallographic and magnetic degrees of freedom and the mechanisms that trigger the field-induced processes in the $Tb_5(Si_xGe_{1-x})_4$ compounds.

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I. INTRODUCTION

$Gd_5(Si_xGe_{1-x})_4$ is a unique class of materials where many important properties and exotic behavior have been recently discovered.[1] The giant magnetocaloric effect,[2,3] strong magnetoelastic effects,[4,5] giant magnetoresistance,[6,7] unusual Hall effect,[8] and spontaneous generation of voltage[9] can be emphasized as the most relevant. This intriguing phenomenology has been associated with the intrinsically layered crystallographic structure combined with a magnetic-martensitic first-order phase transformation.[10] The coupled magnetic-crystallographic transition can be induced reversibly by the change of external parameters such as temperature, an external magnetic field, or hydrostatic pressure.[1–5] Therefore, these alloys are attractive for their potential applications in magnetic refrigeration and/or as magnetostrictive and magnetoresistive transducers.

5:4 pseudobinary compounds with other rare earths are being actively investigated,[11–13] and quite recently, a new $Gd_5(SiSn)_4$ system has also been shown to exist and characterized.[14] In particular, a great deal of effort has been devoted to the $Tb_5(Si_xGe_{1-x})_4$ series.[15–19] In a previous work,[19] we reported the complex magnetic and crystallographic temperature-composition phase diagram of $Tb_5(Si_xGe_{1-x})_4$. The use of neutron diffraction experiments was indispensable to fully characterize the different crystallographic and magnetic phases as a function of temperature. Alloys with intermediate compositions $0.4 \leqslant x \leqslant 0.6$ present a monoclinic (M) structure at room temperature (space group $P112_1/a$). On cooling down, these materials exhibit a first-order crystallographic-magnetic transformation (T_C) to an orthorhombic [$O(\mathrm{I})$, space group $Pnma$] canted ferromagnetic structure (FM): see details in Ref. 19. The aim of this paper is to study the possibility to induce reversibly this magnetostructural transition by applying an external magnetic field above $T_C \cong 110$ K. Magnetostriction and magnetoresistance measurements in $Tb_5Si_2Ge_2$ suggest that, unlike the $Gd_5(Si_xGe_{1-x})_4$ alloys, the field-induced $M \rightarrow O(\mathrm{I})$ transition is not complete even at temperatures close to (and above) T_C. To investigate this point further, new high-intensity and high-resolution neutron diffraction experiments both in zero and in an applied magnetic field have been carried out. This technique has allowed us to discover the existence of a novel monoclinic and ferromagnetic phase (M-FM) in zero field that sets in before (on cooling the sample) the $M \rightarrow O(\mathrm{I})$ structural transformation. This demonstrates that, in $Tb_5(Si_xGe_{1-x})_4$, the structural and magnetic transitions are not fully coupled, the interplay between crystallographic and magnetic degrees of freedom being more complex than previously thought. The behavior under field will be discussed.

II. EXPERIMENT

The $Tb_5Si_2Ge_2$ alloy has been synthesized by arc melting. Details on the material preparation and its characterization can be found elsewhere.[19]

Linear thermal expansion ($\Delta l/l$) measurements were performed using the strain-gauge technique. The electrical resistivity (ρ) experiments were done with a conventional four-probe method (excitation dc current of 5 mA). Magnetostriction and magnetoresistance experiments were performed in a superconducting coil producing steady magnetic fields of up to 120 kOe.

Neutron diffraction experiments were carried out on the high-resolution powder diffractometer D2B ($\lambda = 1.596$ Å and 2.398 Å) and the high-intensity powder diffractometer D1B ($\lambda = 2.52$ Å), both at the ILL, Grenoble. Diffraction patterns were collected between $2\theta = 5°$ and 165° (D2B) at selected temperatures ranging from 85 to 120 K and in magnetic fields up to 50 kOe. The data were analyzed using the Rietveld refinement program FULLPROF[20] which allows a simultaneous refinement of structural and magnetic profiles.

III. RESULTS AND DISCUSSION

Linear thermal expansion experiments revealed a large anomaly at T_C, $\Delta l/l \cong 0.2\%$, associated with the first-order structural transformation from the high-temperature M to the low-temperature $O(\mathrm{I})$ phase.[19] The results have been repro-

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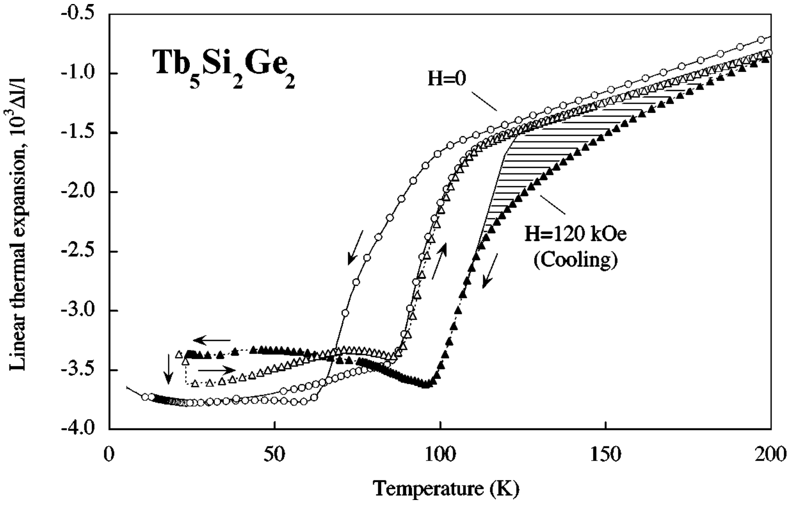

FIG. 1. Linear thermal expansion ($\Delta l/l$) as a function of temperature of $Tb_5Si_2Ge_2$: zero-field run (○), cooling run in a magnetic field of 120 kOe (▲), and zero-field heating run after removal of the field at low temperatures (Δ). The anomalous contribution to $\Delta l/l$ above T_C has been indicated with a striped pattern.

duced in Fig. 1 (open circles). In a second run, the sample was cooled from room temperature in a magnetic field of 120 kOe (block triangles). The field was removed at low temperatures ($\cong 23$ K), a small $\cong 0.02\%$ magnetostrictive effect being seen, and the sample was then allowed to warm up to room temperature (open triangles). Both heating curves in zero field coincide reasonably well. Contrary to the case of $Gd_5(Si_xGe_{1-x})_4$ where a positive shift of the $\Delta l/l$ curve with increasing field was simply observed along the temperature axis,[4] a more complex behavior is seen in $Tb_5Si_2Ge_2$. The departure of the expected behavior has been marked in Fig. 1 with a striped pattern. This points to a more complex magnetic and/or crystallographic behavior above T_C than previously reported. At this point it was thus unclear whether the $M \rightarrow O(\mathrm{I})$ transition could be induced by an isothermal application of a magnetic field above T_C. In order to check this point, we carried out magnetostriction isotherms along the parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) directions to the applied magnetic field, the results being shown in Fig. 2(a). As a major difference with the magnetoelastic behavior of the Gd alloys[4,5,21] where $\lambda_{\parallel} \approx \lambda_{\perp}$, in the case of $Tb_5Si_2Ge_2$ a huge anisotropic effect is seen, i.e., $\lambda_{\parallel} \gg \lambda_{\perp}$. Therefore, we can calculate the volume (ω) and anisotropic magnetostriction (λ_t) as $\omega = \lambda_{\parallel} + 2\lambda_{\perp}$ and $\lambda_t = \lambda_{\parallel} - 2\lambda_{\perp}$ the thermal dependence at the maximum applied field of 120 kOe is displayed in Fig. 2(b). It is noteworthy that the maximum volume magnetostriction amounts to ω (105 K, 120 kOe) $\cong -0.14\%$ whereas the spontaneous volume expansion taken from Fig. 1 can be estimated as $\Delta V/V = 3\Delta l/l \cong -0.6\%$. In addition, this value falls down quite rapidly on increasing the temperature: see Fig. 2(b). The shape of the isotherms is also intriguing, a huge hysteresis and no clear metamagnetic behavior being observed: just a smooth change in slope is detected around 90–100 K in our available range of magnetic fields. From the observed behavior we can anticipate that some structural transition might be taken place, but that the transformation is probably incomplete and takes place over a more extended magnetic field range than in similar Gd alloys.[4,5,21] In addition, the huge anisotropic effect λ_t (100 K, 120 kOe) $\cong -0.12\%$ points to an active role of the highly anisotropic Tb^{3+} ions.

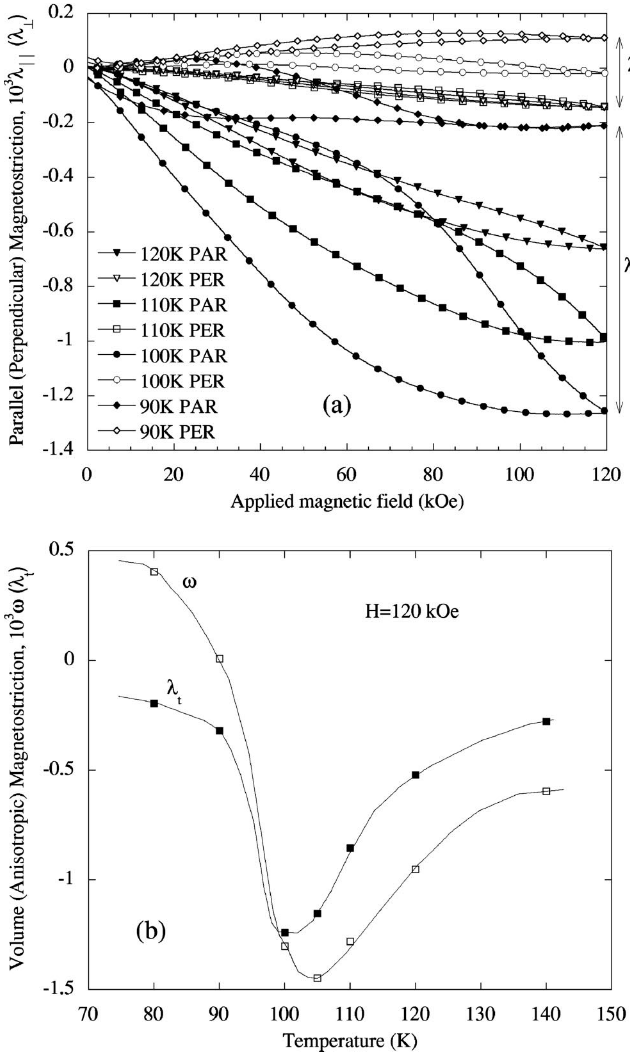

FIG. 2. (a) Magnetostriction isotherms of $Tb_5Si_2Ge_2$ along the parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) directions to the applied magnetic field at some selected temperatures. (b) Temperature dependence of the volume ($\omega = \lambda_{\parallel} + 2\lambda_{\perp}$) and anisotropic ($\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$) magnetostriction at the maximum applied field of 120 kOe. Lines are guides to the eye.

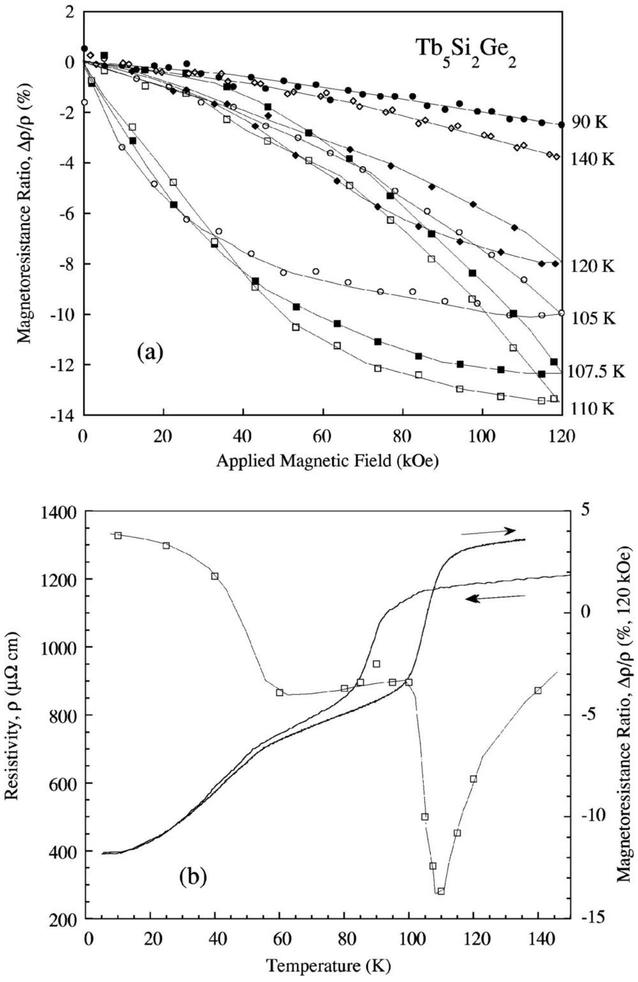

FIG. 3. (a) Magnetoresistance ratio $\Delta\rho/\rho$ as a function of the applied magnetic field at some selected temperatures in the $T = 90-140$ K range. (b) Temperature dependence of the magnetoresistance of Tb$_5$Si$_2$Ge$_2$ at the maximum applied field of 120 kOe (□) and zero-field electrical resistivity (ρ). Lines are guides to the eye.

In order to make our case stronger, we also carried out magnetoresistance isotherms $\Delta\rho/\rho(H) = [\rho(H) - \rho(0)]/\rho(0)$ in the whole temperature range. We display in Fig. 3(a) some selected temperatures and the evolution of the maximum magnetoresistance ratio $\Delta\rho/\rho$ (120 kOe) together with the spontaneous resistivity data from Ref. 19 in Fig. 3(b). A huge drop is seen at T_C in the resistivity data, $\Delta\rho/\rho \cong -30\%$, but in agreement with the previously discussed magnetostriction results, the maximum magnetoresistance ratio only amounts to $\Delta\rho/\rho$ (110 K, 120 kOe) $\cong -14\%$, the hysteresis is abnormally large, and no clear metamagnetic transition is observed. A change in the temperature dependence of the magnetoresistance ratio is observed below ≈ 60 K [Fig. 3(b)] together with a change in slope in the resistivity data. We can associate this effect with the spin reorientation transition observed at this temperature.[19]

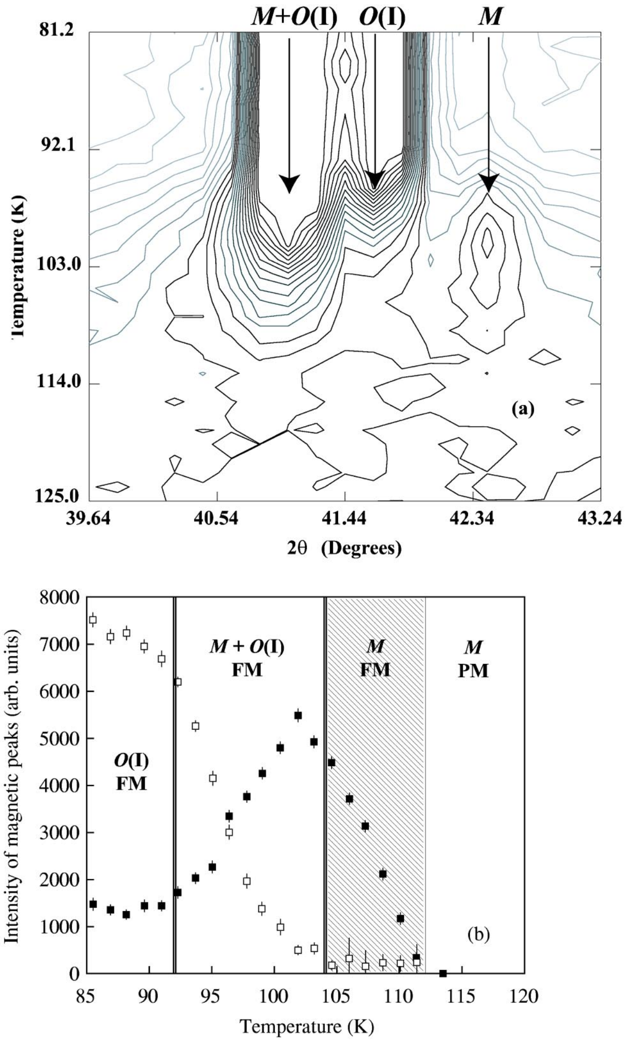

FIG. 4. (a) Neutron diffraction contour plot of Tb$_5$Si$_2$Ge$_2$ in a selected angular and temperature range as recorded in the high-intensity D1B diffractometer. The diffraction peaks marked are of pure magnetic origin coming from the M, O(I), or both [$M + O$(I)] crystallographic structures. (b) Temperature dependence of the intensity of selected O(I) (□) and $M + O$(I) (■) diffraction peaks as determined from D1B data. The newly discovered M-FM phase has been indicated with a striped pattern. A single vertical line marks the onset of long-range FM and the double vertical lines the $M \leftrightarrow O$(I) structural transformation. This experiment was performed on cooling the sample.

To confirm the presumed existence of an incomplete and smooth field-induced structural transition, we decided to perform high-resolution neutron powder diffraction experiments in an applied magnetic field (D2B) as the most relevant tool to probe simultaneously both changes in the crystallographic and magnetic structure. Since the strongest effects are confined close to T_C (Figs. 2 and 3) and the maximum field in our experimental setup was 50 kOe, we first carried out a detailed thermal scan on the high-intensity D1B diffractometer in the reduced 80–125 K range in order to locate exactly the transition temperatures. Unexpectedly, we discovered a magnetic phase that was overlooked in previous experiments.[19] This is shown in a contour plot [see Fig. 4(a)] in a selected angular range. The marked diffraction peaks are of pure magnetic origin coming from the M, O(I), or both

$[M+O(\mathrm{I})]$ crystallographic structures. It is easily seen that magnetism in the M phase sets in at about 114 K before we have any noticeable amount of $O(\mathrm{I})$ phase. The structural $M \rightarrow O(\mathrm{I})$ transformation and the accompanying upcoming magnetic peaks start at a lower temperature $\cong 105$ K. We must underline that this experiment was performed cooling the sample. In Fig. 4(b) we display the thermal evolution of the integrated intensity of a purely magnetic $O(\mathrm{I})$ peak (open squares) together with that of another reflection with a strong magnetic contribution from the M phase (block squares). The double vertical lines delimit the structural $M \leftrightarrow O(\mathrm{I})$ transformation and the single vertical line the onset of long-range ferromagnetism. The new monoclinic-ferromagnetic phase has been marked (striped pattern). In order to determine the magnetic structure of the M-FM phase, we carried out Rietveld refinement of a spectrum at 108 K, i.e., at a temperature where no $O(\mathrm{I})$ phase was present [see Fig. 4(b)]. Our fit revealed the structure to be mainly ferromagnetic along the a axis, with a small canting ($\approx 10°$ averaged over the different Tb sites) along the b axis.

We believe that the discovery of long-range ferromagnetism in the monoclinic $P112_1/a$ crystallographic structure is an extremely relevant piece of information that should be taken into account in any theoretical approach of the behavior of the 5:4 system. All three crystallographic structures present in the 5:4 alloys [M, $O(\mathrm{I})$, $O(\mathrm{II})$] (Ref. 22) are composed of identical two-dimensional subnanometer-thick layers (slabs) interconnected via partially covalent interslab X-X bonds ($X=$Si,Ge). In the $O(\mathrm{I})$ structure, all the slabs are interconnected by X-X bonds; half of these bonds are broken in the M structure and none remain in the $O(\mathrm{II})$ structure. The magnetic-crystallographic transition involves breaking and reforming of specific covalent X-X bonds,[10] and the low-temperature ground state for all compositions $0<x\leqslant 1$ is always FM with all the slabs being interconnected, i.e., with the $O(\mathrm{I})$ structure.[5,10,19] Our results demonstrate that the M structure with half of the interslab bonds still intact can support long-range ferromagnetism, at least in the $\mathrm{Tb}_5(\mathrm{Si}_x\mathrm{Ge}_{1-x})_4$ compounds.

The presence of the M-FM phase might also have a strong impact on the effect of a magnetic field when applied above the structural transformation. We have carried out high-resolution (D2B) neutron diffraction experiments at selected temperatures ($T=100$, 105, 110, 115, and 120 K) and in fields of up to 50 kOe. The fits are complicated due to the number of different crystallographic and magnetic phases involved. The main simplification made in the fits was to consider the magnetic moment values in the orthorhombic $O(\mathrm{I})$ phase independent of the applied magnetic field and temperature. This is plausible since the ordering temperatures of the Si-rich $\mathrm{Tb}_5(\mathrm{Si}_x\mathrm{Ge}_{1-x})_4$ alloys with a room-temperature $O(\mathrm{I})$ structure are much higher. Nevertheless, we confirmed our assumption by comparing the magnetic moment values at 85 K [100% $O(\mathrm{I})$ phase], $8.53(9)\mu_B$, $7.81(7)\mu_B$, and $8.08(7)\mu_B$ (for Tb1, Tb2, and Tb3) (see Table V in Ref. 19) with those at 105 K and in 50 kOe, the results coinciding within the experimental error. As a main outcome of our fits, we show in Fig. 5(a) the percentage of the $O(\mathrm{I})$ phase at the selected temperatures as a function of applied magnetic field. Our results demonstrate that the magnetic-field-induced $M \rightarrow O(\mathrm{I})$ transformation indeed takes place, but the field effect is highly inefficient. Even at temperatures right at T_C such as 105 K [note we just have $\approx 6\%$ of the $O(\mathrm{I})$ phase in zero field], a field of 50 kOe is only able to induce $\approx 50\%$ of the structural change. On increasing the temperature, the percentage of induced $O(\mathrm{I})$ phase in 50 kOe decreases exponentially, amounting to less than 10% at temperatures already in the M-PM phase, i.e., $T \geqslant 115$ K. Another important observation from our neutron diffraction results is nonunifor-

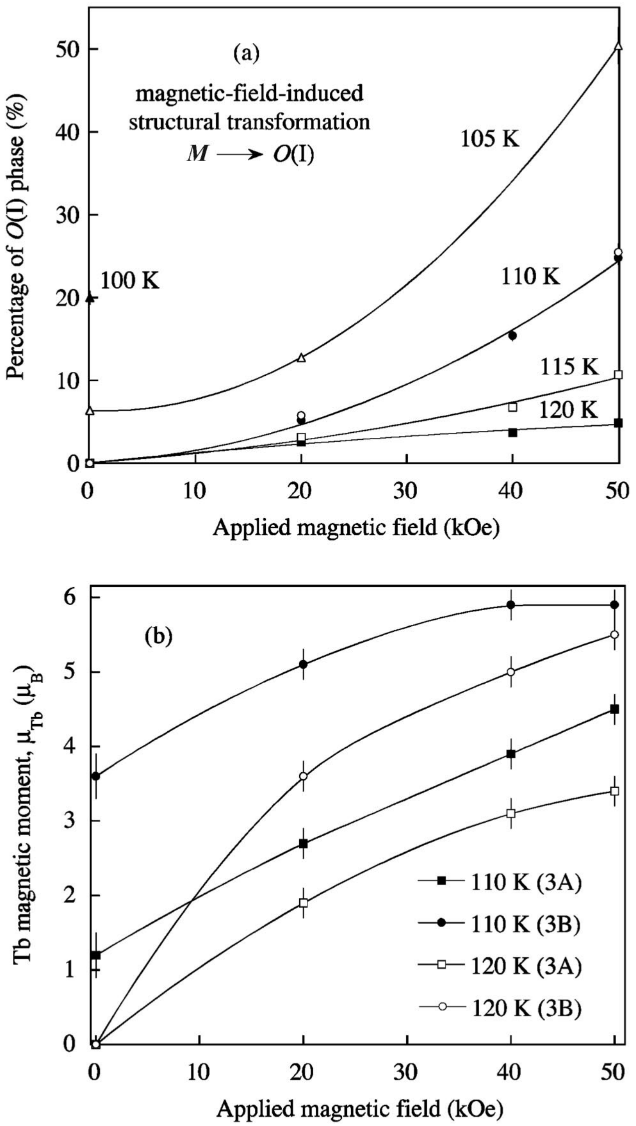

FIG. 5. (a) Magnetic-field dependence of the percentage of $O(\mathrm{I})$ phase at selected temperatures as determined from Rietveld refinements of high-resolution D2B data. (b) Evolution of the Tb magnetic moments at sites 3A and 3B (see Ref. 19 for details) at selected temperatures of 110 K (M-FM) and 120 K (M-PM) as a function of the applied magnetic field.

mity of the values of the ferromagnetic moments in the monoclinic phase over the different Tb ions in the unit cell. For instance, at 110 K and zero field, the fit yield values of $4.0(3)\mu_B$, $1.2(3)\mu_B$, $4.2(3)\mu_B$, $1.2(3)\mu_B$, and $3.6(3)\mu_B$ for the Tb1, Tb2A, Tb2B, Tb3A, and Tb3B sites. The definition and precise atomic coordinates can be consulted in Ref. 19. It is interesting to note that the ferromagnetic moments at the Tb2A and Tb3A positions are much smaller than the rest. These ions are precisely the ones closer to the X-X broken bonds and, therefore, the absence of covalent X-X bonds should favor a decrease in the local exchange interaction producing magnetic frustration.[10,23,24] In Fig. 5(b) we display the magnetic-field dependence of the selected Tb3A and Tb3B ions at two selected temperatures, 110 K (M-FM phase) and 120 K (M-PM phase), where the differences between these sites is clearly seen. In the M-FM phase the behavior is as expected for a ferromagnet: the moment values increase slowly with field. An interesting effect is also seen at 120 K in the M-PM phase. A field of 20 kOe is sufficient to induce long-range ferromagnetism in this alloy, and therefore, a field-induced M-PM$\rightarrow M$-FM transition is taking place concomitant with the structural $M \rightarrow O(\mathrm{I})$ transformation [Fig. 5(a)]. We must underline that this anisotropy does not exist between the Tb magnetic moments at different sites in the $O(\mathrm{I})$ phase (see moment values in Ref. 19). Unluckily, neutron diffraction studies in $\mathrm{Gd}_5(\mathrm{Si}_x\mathrm{Ge}_{1-x})_4$ are not feasible due to the huge neutron absorption cross section of Gd and the prohibitively expensive price of a suitable isotope. Therefore, our result so far cannot be generalized to other 5:4 systems. Neutron diffraction experiments in other $R_5(\mathrm{Si}_x\mathrm{Ge}_{1-x})_4$ materials are in progress in order to probe the existence of this M-FM phase and the role of the R ion.

IV. SUMMARY

In summary, we have carried out magnetoelastic and magnetoresistance measurements of $\mathrm{Tb}_5\mathrm{Si}_2\mathrm{Ge}_2$. Our results suggest that the magnetic-martensitic transition in this system cannot be induced completely above the transition temperature by isothermal application of an external magnetic field. Neutron powder diffraction experiments were performed to investigate further this intriguing behavior. We have discovered that long-range ferromagnetism sets in the monoclinic $P112_1/a$ structure on cooling down before the structural transformation into the orthorhombic $Pnma$ takes place. This M-FM magnetic structure is mostly collinear along the a axis with partially frustrated Tb magnetic moments at sites close to broken covalent X-X bonds. Neutron data have confirmed that the field-induced $M \rightarrow O(\mathrm{I})$ structural transformation does take place but is incomplete even at temperatures close to T_C. Our results point to the existence of two structural and magnetic phases [M-FM and $O(\mathrm{I})$-FM] in $\mathrm{Tb}_5\mathrm{Si}_2\mathrm{Ge}_2$ close in energy around 105 K. Since both phases are ferromagnetic, the applied magnetic field is quite inefficient in producing a transition between them.

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