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# Magnetostructural properties of $Ho_5(Si_{0.8}Ge_{0.2})_4$

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The magnetostructural properties of $Ho_5(Si_{0.8}Ge_{0.2})_4$ have been investigated both experimentally and by using first-principles theory. The compound orders ferromagnetically at 50 K, and in the temperature range of 50–100 K it exhibits a Griffiths phaselike behavior. The dc magnetization, heat capacity, and the relaxation and frequency dependence of the ac susceptibility indicate that the long-range magnetic order and a spin-glasslike state may coexist in $Ho_5(Si_{0.8}Ge_{0.2})_4$ over a certain temperature range below $T_C$. Despite adopting the $Gd_5Si_2Ge_2$-type monoclinic (M-type) structure at room temperature, the compound does not exhibit a magnetostructural transition at $T_C$, unlike some other members of the $R_5(Si_{1-x}Ge_x)_4$ series with $R$=Gd, Tb, and Dy. The tight-binding linear muffin-tin orbital calculations within the local spin-density approximation show that in $R_5(Si_{1-x}Ge_x)_4$ compounds the gain in the exchange energy brought about by the M-type to $Gd_5Si_4$-type orthorhombic (O-I) transformation decreases as $R$ is changed from Gd to other heavy lanthanides and the absence of the M to O-I phase transformation in $Ho_5(Si_{0.8}Ge_{0.2})_4$ is a result of low gain in the magnetic contribution to the total energy.

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## I. INTRODUCTION

A large variety of interesting magnetic behaviors exhibited by rare-earth ($R$)-based intermetallic compounds makes them a unique playground for fundamental studies, as well as for applications based on magnetostriction, magnetoresistance, magnetocaloric, and other effects.[1–6] Among various classes of rare-earth-based intermetallics, the so-called 5:4 compounds formed by the rare earth and nonmagnetic group 14 elements are recently drawing considerable attention of various research groups.[7–26] Owing to the unusual sensitivity of their crystal structures to applied magnetic field, many members of the $R_5(Si_{1-x}Ge_x)_4$ family exhibit field-driven magnetostructural transitions (MSTs), which underlie the accompanying giant magnetoresistance (GMR), giant magnetocaloric effect (GMCE), and strong magnetoelastic effect.[3,4,8–10,14,15,18] The presence of GMCE, GMR, and large magnetoelastic effects makes this family of compounds promising for applications such as magnetic refrigeration, magnetoresistive sensors, and/or magnetostrictive transducers.

The $R_5(Si_{1-x}Ge_x)_4$ compounds adopt layered crystal structures made up of nanoscale slabs; each slab consists of five monolayers of $R$ and Si/Ge atoms. Flexible arrangements of these slabs controlled via varying Si/Ge-Si/Ge interslab bonds gives rise to three different crystal structures, namely, the $Gd_5Si_4$-type (space group *Pnma*; also referred as the O-I type), $Gd_5Si_2Ge_2$-type structure (space group $P112_1/a$; M type), and $Sm_5Ge_4$-type (space group *Pnma*; O-II type), exhibited by this series of alloys.[18] In the O-I type structure, all of the slabs are connected through strong Si/Ge-Si/Ge bonds, whereas in the O-II type, these interslab bonds are much longer, and therefore, weaker. In the M-type structure, the strong and weak interslab Si/Ge-Si/Ge bonds alternate from one slab to another. Therefore, for a same $R$ element, the $R_5(Si_{1-x}Ge_x)_4$ phase with the O-I structure always has the lowest unit-cell volume, whereas the one with the O-II structure has the largest unit-cell volume. In the M-type structure, the unit-cell volume is intermediate between those of O-I and O-II structures. It has been shown experimentally that the interslab Si/Ge-Si/Ge bonds are sensitive to the chemical composition, both to the nature of the $R$ element and to the ratio of Si and Ge atoms $[(1-x)/x]$, temperature, magnetic field, and/or pressure.[8,9,14,15] Therefore, it is the field-driven rearrangement in the interslab Si/Ge-Si/Ge bonds which leads to field-induced MST's in the $R_5(Si_{1-x}Ge_x)_4$ alloys.[11,15,20,21] These changes in the interslab bonding strongly affect exchange interactions among the interslab $R$ ions.[27–30]

Though the discovery of the GMCE in $Gd_5Si_2Ge_2$ led to an extensive research on the Gd-based $R_5(Si_{1-x}Ge_x)_4$ alloys,[18] in order to better understand the generalities of structure-magnetism relationships, the alloys with other rare earths have also been probed.[9,14,20,21,23] These investigations revealed that MST's are observed in $R_5(Si_{1-x}Ge_x)_4$ compounds with $R$ elements other than Gd. However, in contrast with the Gd-based alloys, $R_5(Si_{1-x}Ge_x)_4$ compounds formed by heavy lanthanides other than Gd exhibit a tendency toward decoupling of structural transformations from the ferromagnetic or ferromagneticlike ordering transitions, and the structural transitions may become incomplete. For example, in the Gd-based compounds the structural transitions are nearly complete (~93%), whereas only ~80%, ~47%, and even 0% completion was reported for $R$=Tb, Dy, and Er, respectively.[11,20,21,28] Moreover, in the Gd-based compounds the ferromagnetic ordering and structural transformations are coupled whereas in the case of Tb and Dy compounds these are separated by ~10 K and 24 K, respectively.

Here we report on the magnetic, magnetocaloric, and crystallographic properties of $Ho_5(Si_{0.8}Ge_{0.2})_4$. The com-

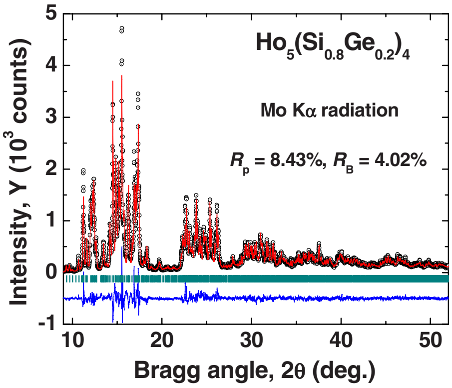

FIG. 1. (Color online) The Rietveld refined room-temperature x-ray diffraction pattern of $Ho_5(Si_{0.8}Ge_{0.2})_4$. In the figure, the open circles represent experimental data points whereas lines through them represent the calculated pattern. The calculated positions of the Bragg peaks are shown as vertical bars and the differences between the observed and calculated intensities are shown at the bottom of the plot.

TABLE I. Crystallographic data of $Ho_5(Si_{0.8}Ge_{0.2})_4$ at 293 K.

$T$=293 K; space group $P112_1/a$; $a$=7.4258(3) Å, $b$=14.5054(6) Å, $c$=7.6228(3) Å, $\gamma$=93.021(2)°

| | | | | |
|---|---|---|---|---|
| Ho1 | −0.0078(4) | 0.5997(2) | 0.1780(5) | 1.000 |
| Ho2 | 0.0137(4) | 0.9035(2) | 0.1820(5) | 1.000 |
| Ho3 | 0.3323(4) | 0.1215(2) | 0.1751(4) | 1.000 |
| Ho4 | 0.3607(4) | 0.3825(2) | 0.1691(4) | 1.000 |
| Ho5 | 0.1809(4) | 0.2494(2) | 0.5035(4) | 1.000 |
| Si1A | 0.159(2) | 0.0406(8) | 0.487(2) | 0.84(2) |
| Si1B | 0.204(2) | 0.4604(8) | 0.485(2) | 0.77(2) |
| Si2 | 0.030(2) | 0.252(1) | 0.095(2) | 0.97(1) |
| Si3 | 0.293(1) | 0.2516(6) | 0.871(1) | 0.54(2) |
| Ge1A | 0.159(2) | 0.0406(8) | 0.487(2) | 0.16(2) |
| Ge1B | 0.204(2) | 0.4604(8) | 0.485(2) | 0.23(2) |
| Ge2 | 0.030(2) | 0.252(1) | 0.095(2) | 0.03(1) |
| Ge3 | 0.293(1) | 0.2516(6) | 0.871(1) | 0.46(2) |

pound adopts the $Gd_5Si_2Ge_2$-type monoclinic structure in the paramagnetic state, but unlike many other $R_5(Si_{1-x}Ge_x)_4$ alloys with the M-type structure at room temperature, $Ho_5(Si_{0.8}Ge_{0.2})_4$ does not exhibit any structural transitions as the temperature is lowered. Magnetization data show that the title compound orders ferromagnetically at 50 K, and between 50 and 100 K it exhibits a negative deviation from the Curie-Weiss behavior, which is a hallmark of the Griffiths phase.[17,31] Relaxation and frequency-dependent ac susceptibility data suggest that the compound exhibits spin-glasslike features below 50 K. Analysis of magnetocaloric properties implies that $Ho_5(Si_{0.8}Ge_{0.2})_4$ is a suitable material for magnetic refrigeration around 50 K. First-principles calculations show that low gain of the exchange energy is the reason for the absence of the structural rearrangement in the title compound.

## II. EXPERIMENTAL DETAILS

The $Ho_5(Si_{0.8}Ge_{0.2})_4$ alloy weighing 5 g was prepared by arc melting of stoichiometric amounts of the constituent elements on a water-cooled copper hearth under argon atmosphere. To ensure homogeneity, the ingot was turned over and remelted six times. The Ho used was prepared by the Material Preparation Center[32] of the Ames Laboratory and it was 99.68 at. % (99.98 wt %) pure with respect to all other elements in the periodic table. The metal had following major impurities in the parts per million (ppm) atomic (and ppm weight): O—788 (77); C—2261 (165), and N—153 (13). The Si and Ge were obtained from Cerac Inc., USA and were better than 99.999 wt % pure.

Figure 1 shows the room-temperature x-ray powder-diffraction data of $Ho_5(Si_{0.8}Ge_{0.2})_4$. The Rietveld refinement of the x-ray diffraction (XRD) pattern was carried out using LHPM-RIETICA.[33] The refinement reveals that $Ho_5(Si_{0.8}Ge_{0.2})_4$ is a single phase compound crystallizing in the $Gd_5Si_2Ge_2$-type monoclinic structure. The room-temperature crystallographic parameters of $Ho_5(Si_{0.8}Ge_{0.2})_4$ are given in Table I. The refinement of populations of the Si and Ge sites with the only restriction that all corresponding sites are fully occupied leads to $Ho_5(Si_{0.78\pm0.02}Ge_{0.22\pm0.02})_4$ stoichiometry, which is nearly identical to the as weighed composition.

Magnetic properties were investigated using a superconducting quantum interference device magnetometer, model MPMS XL from Quantum Design, Inc., USA. The temperature ($T$) dependencies of magnetization ($M$) were collected under zero-field-cooled (ZFC) heating, FC cooling (FCC), and FC warming (FCW) conditions. In the ZFC protocol, the sample was cooled to the desired temperature in zero magnetic field and the $M(T)$ data were collected on warming after the application of the field. In the FCC mode, the field was applied at room temperature, and $M(T)$ data were collected during cooling. In the FCW protocol, the sample was cooled in the presence of the field, and the $M(T)$ data were collected during heating of the sample. Relaxation measurements were performed after cooling the sample from 150 K to the desired temperature under ZFC condition. After reaching the target temperature, a field of 10 kOe was turned on for 5 min and the time dependence of magnetization was measured immediately after the field was turned off.

An adiabatic heat pulse calorimeter[34] was employed to measure temperature dependencies of heat capacity ($C$) under various applied magnetic fields. Temperature (5–300 K) dependent x-ray powder-diffraction data were collected on a Rigaku TTRAX powder diffractometer using Mo $K\alpha$ radiation in the $2\theta$ range of $9°-52°$.[35] The sample for XRD was prepared as described in Ref. 35.

## III. EXPERIMENTAL RESULTS AND DISCUSSIONS

### A. Magnetic and magnetocaloric properties

Figure 2 shows the temperature dependencies of magnetization ($M$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ measured in an applied field ($H$) of 50 Oe under ZFC, FCC, and FCW conditions. A ferromagneticlike transition occurs at $T_C$ of 50 K. Additional magnetic anomalies may also be seen at 23 K ($T_1$) and 7 K

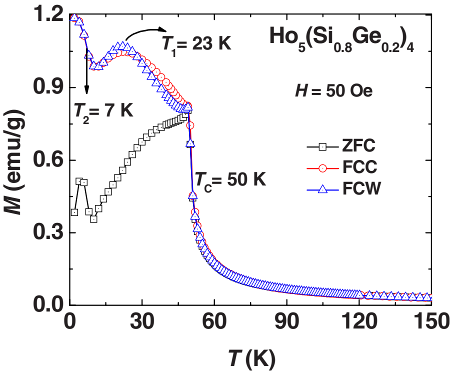

FIG. 2. (Color online) The temperature ($T$) dependencies of the magnetization ($M$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ measured in an applied field ($H$) of 50 Oe under zero-field-cooled (ZFC), FC cooling (FCC), and FC warming (FCW) conditions.

($T_2$). These low-temperature anomalies are consistent with previous reports[23,36–38] on other $Ho_5(Si_{1-x}Ge_x)_4$ alloys, and they may be attributed to spin reorientation transitions resulting from a competition between magnetic exchange and crystalline electric field.[1] We note that although the magnetic anomalies at $T_2$ and $T_C$ are clearly seen in all of the $M(T)$ data, the magnetic anomaly at $T_1$ is broad and is only visible in the FCC and FCW data.

Another feature worth noting in Fig. 2 is a large thermomagnetic irreversibility between the ZFC and FCC/FCW $M(T)$ data. The irreversibility between the ZFC and FCC/FCW data is a typical feature associated with a large anisotropy of a ferromagnet or the formation of a spin glass or the coexistence of ferromagnetic and antiferromagnetic interactions or with random orientations of crystallites of an antiferromagnet.[39–42] Ferromagnets with large anisotropy and low ordering temperature usually have narrow domain walls and the irreversibility arises due to pinning of the walls.[40,41] In the ZFC mode and in low magnetic fields, the motions of the domain walls are hindered by the energy barriers provided by the pinning centers, which results in a small magnetization at low temperatures. When temperature increases, the thermal activation of the walls leads to an increase in the magnetization. This increase in the magnetization due to the thermal activation of domain walls is likely the reason for the absence of the clear magnetic anomaly at $T_1$ in the ZFC $M(T)$ data mentioned above.

During the FCC/FCW measurements the magnetic field is applied in the paramagnetic state and, therefore, the domain walls move in the direction of the field as the sample is cooled through $T_C$, thereby resulting in a high value of magnetization at low temperatures. In view of the low $T_C$ and large magnetocrystalline anisotropy associated with many of the $R_5(Si_{1-x}Ge_x)_4$ compounds,[43–45] $Ho_5(Si_{0.8}Ge_{0.2})_4$ may also be considered a narrow domain-wall system and the thermomagnetic irreversibility may be attributed to domain-wall pinning effects. The role of pinning is further confirmed by $M(T)$ data measured in 200 Oe and 1 kOe magnetic fields (not shown). For $H=50$, 200 Oe and 1 kOe, the bifurcation temperature between the ZFC and FCC/FCW data decreases from 49 K to 42 K and to 35 K, respectively; this systematic reduction in temperature supports the domain-wall pinning mechanism.[46] Furthermore, due to a long-range oscillatory nature of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, the rare-earth-based intermetallic compounds often exhibit competing interactions[22,47] and, therefore, the irreversibility between ZFC and FCC/FCW $M(T)$ data may also have some contribution from intrinsic frustration of a complex spin system, which the title compound indeed is. Magnetic frustration was deemed a primary reason for a similar irreversibility between the ZFC and FCC/FCW data in other intermetallic compounds.[22,40,48,49]

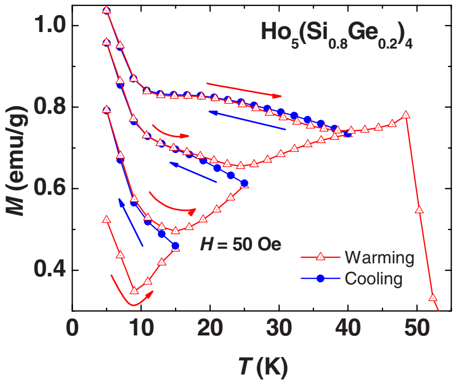

FIG. 3. (Color online) Metastability and path dependence of the magnetization ($M$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$.

As follows from Fig. 2, the FCC and FCW $M(T)$ data also show weak irreversibility. Generally, such irreversibility is observed in materials exhibiting first-order transitions; however, it has been shown recently that such behavior may also be observed in compounds with frustrated spins.[22,49] The heat capacity and the temperature-dependent x-ray studies (see below) show that $Ho_5(Si_{0.8}Ge_{0.2})_4$ does not undergo a first-order transition and, therefore, the irreversibility between the FCC and FCW $M(T)$ data is likely a consequence of a metastable magnetic ground state of the compound. In order to clarify the low-temperature magnetic state, $M(T)$ data were measured for various thermal cycling conditions and the results are shown in Fig. 3. Initially the sample was cooled to 5 K in the ZFC mode, and the magnetization was measured from 5 to 15 K in a 50 Oe magnetic field. Subsequently, the magnetization was measured when temperature was cycled back from 15 to 5 K and, then from 5 to 25 K, 25 to 5 K, 5 to 40 K, 40 to 5 K, and 5 to 70 K. We note that in the ordered state the magnetization depends upon the start temperature. Thus, these results suggest that the magnetic ground state of the title compound has a metastable character.

Figure 4 shows the temperature dependence of the inverse magnetic susceptibility ($H/M$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ and the Curie-Weiss $[M/H=C/(T-\theta_P)]$ fit to the experimental data. Above 100 K, the susceptibility obeys Curie-Weiss law and yields Weiss temperature ($\theta_P$) of 35 K and the effective moment ($P_{eff}$) of $10.5\mu_B/Ho^{3+}$. The experimentally determined value of $P_{eff}$ compares well with the $Ho^{3+}$ free ion value, $g[J(J+1)]^{1/2}$, of $10.6\mu_B$. The positive value of $\theta_P$ indicates that ferromagnetic interactions are dominant. We note that though the $\theta_P$ is positive, it is smaller than the ferromagnetic ordering temperature ($T_C=50$ K). Therefore, these observa-

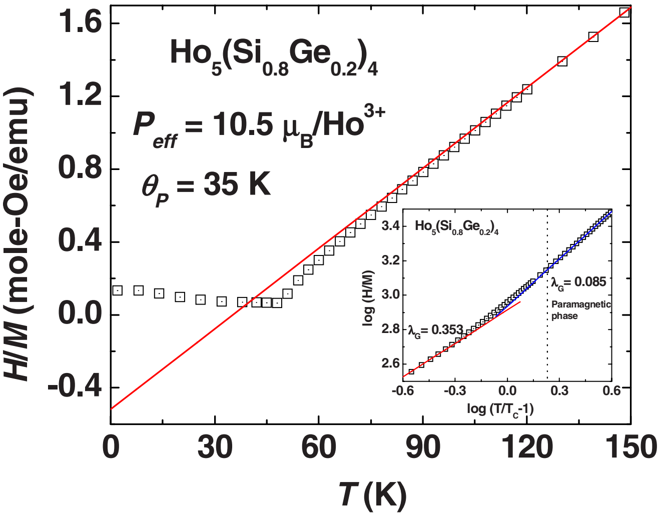

FIG. 4. (Color online) Temperature dependence of the inverse magnetic susceptibility $(H/M)$ of $\mathrm{Ho_5(Si_{0.8}Ge_{0.2})_4}$ measured in 50 Oe magnetic field. The line through the points shows the Curie-Weiss fit to the susceptibility. The inset shows the linear fits of $\log(H/M)$ vs $\log(T/T_C-1)$ to determine λ in $H/M \propto (T-T_C)^{1-\lambda}$.

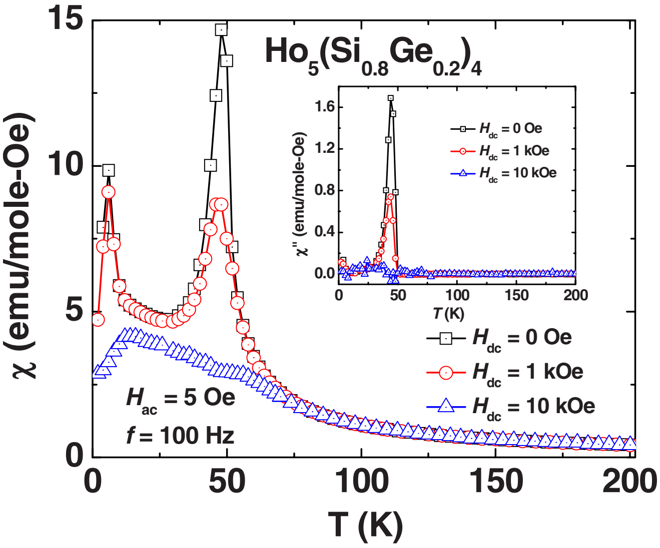

FIG. 5. (Color online) Temperature dependencies of the real component of ac susceptibility $(\chi')$ of $\mathrm{Ho_5(Si_{0.8}Ge_{0.2})_4}$ collected under various dc bias fields $(H_{dc})$. The inset shows the temperature variation of the imaginary component of the ac susceptibility $(\chi'')$.

tions indicate that despite of the predominant ferromagnetic interactions, antiferromagnetic correlations are also present in the title compound.[50] The competition between the ferromagnetic and antiferromagnetic interactions may be the reason for magnetic frustration, and thus, for the thermomagnetic irreversibility and the metastability of the magnetic ground state mentioned above.

Between $T_C$ and 100 K, the inverse susceptibility shows a negative deviation from the Curie-Weiss behavior, which is often considered as a signature of a Griffiths-type phase.[17] The Griffiths phase is defined as an intermediate magnetic state between a true paramagnetic state and a ferromagnetically ordered state where the magnetization ceases to be an analytical function of magnetic field when the field approaches zero,[31] and is usually observed in materials with competing magnetic interactions.[17,51] Competing interactions lead to ferromagnetic clustering, thereby resulting in a negative deviation from the Curie-Weiss law. We note that the ordering temperature of the Si-rich members of $\mathrm{Ho_5(Si_{1-x}Ge_x)_4}$ series is strongly dependent upon Si concentration,[23] and therefore, local variations in the Si concentration may lead to considerable changes in the exchange interactions at the microscopic or nanoscale level. It has been reported that in $\mathrm{Gd_5Si_2Ge_2}$, which is isostructural with the title compound, the microscopic atomic rearrangements caused by the heat treatment affect the Curie temperature.[52] Thus, apart from the long-range oscillatory nature of RKKY interaction, competing interactions arising from the microscopic or nanoscale compositional variations may also play a role in the formation of ferromagnetic clusters in the title compound. In the paramagnetic regime the stacking faults arising from the microtwinning [reported in the isostructural compound $\mathrm{Gd_5Si_2Ge_2}$ (Ref. 53)] may provide nucleation centers for the ferromagnetic clusters to precipitate in the paramagnetic matrix. Based on the small-angle neutron-scattering experiments, Magen *et al.*[17] showed that in the isostructural $\mathrm{Tb_5Si_2Ge_2}$, the local compositional variations in Si/Ge ratio and the disorder due to the microtwinning lead to the formation of ferromagnetic nanoclusters in the paramagnetic regime.

In the Griffiths-type phase regime, the magnetic susceptibility can be represented as $H/M\alpha\ (T-T_C)^{1-\lambda}$ with $0<\lambda \leq 1$.[17,51,54] As shown in the inset of Fig. 4, $\lambda=0.353$ for temperature ranging between 60 and 80 K and $\lambda=0.086$ in the paramagnetic region. These λ values compare well with those reported for other $R_5(\mathrm{Si}_{1-x}\mathrm{Ge}_x)_4$ compounds.[17,51]

The temperature dependence of the real component of the ac susceptibility $(\chi')$ collected under various dc bias fields $(H_{dc})$ is shown in Fig. 5 and the imaginary part $(\chi'')$ is shown in the inset of Fig. 5. Although the magnetic anomalies associated with the magnetic ordering at $T_C=50$ K and the spin reorientation occurring at $T_2(7$ K) are clearly seen in the $\chi'(T)$ measured under dc bias field $(H_{dc})$ of 0 and 1 kOe, they are suppressed in $H_{dc}=10$ kOe. The anomaly associated with the magnetic transition at $T_1=23$ K; see Fig. 2 is not observed in the $\chi'(T)$ data. It is well known that in a ferromagnetic material, the measured ac susceptibility is a result of interaction of magnetic field with magnetic domains and, in the presence of a dc bias field, the response of domains is suppressed.[55] Therefore, it appears that large changes occurring in the susceptibility due to domain-wall motions in $H_{dc}$ of 0 and 1 kOe hide the changes in susceptibility brought about by the modified magnetic structure at $T_1$. This observation is consistent with the difficulties in discerning the $T_1$ transition in low-field ZFC $M(T)$ data discussed above.

The imaginary component of ac susceptibility shows a peak near $T_C$ and the peak value decreases with increasing bias field. Usually a finite value of $\chi''$ reflects an energy loss process and, owing to energy losses associated with the domain-wall motion, a peak in the $\chi''(T)$ data is observed in ferromagnetic materials.[22,56] Therefore, the peak in $\chi''(T)$ near $T_C$ confirms that $\mathrm{Ho_5(Si_{0.8}Ge_{0.2})_4}$ is predominantly fer-

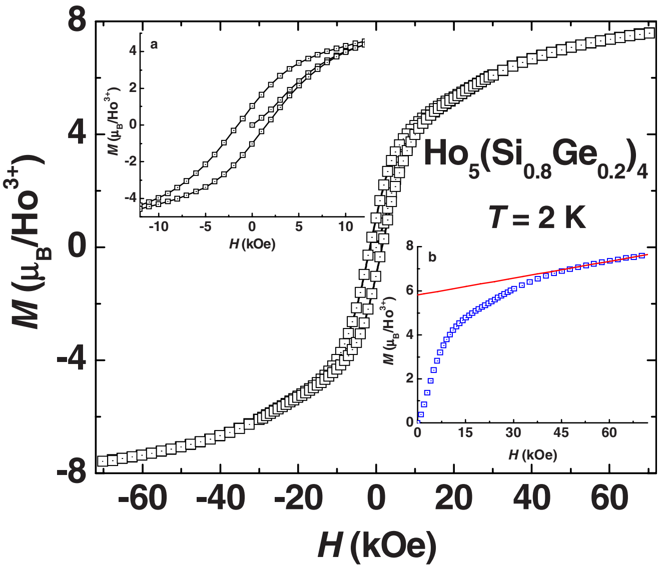

FIG. 6. (Color online) Field ($H$) dependence of the magnetization ($M$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ measured at $T=2$ K. The upper inset (a) shows the low-field details whereas the lower inset (b) shows the $M(H)$ data for increasing field and a linear fit to high-field data.

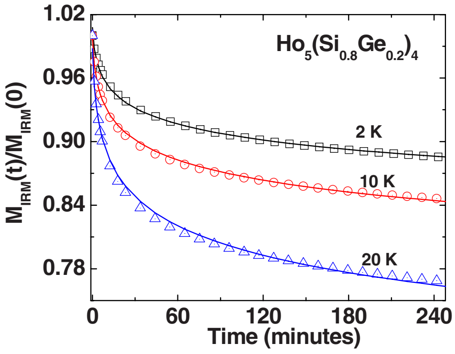

FIG. 7. (Color online) Time ($t$) dependencies of isothermal remanent magnetization $[M_{\mathrm{IRM}}(T,t)]$ normalized to the value at $t=0$ $[M_{\mathrm{IRM}}(T,0)]$ of $Ho_5(Si_{0.8}Ge_{0.2})_4$. The open symbols represent the experimental data points whereas the lines through them are fits of equation $M_{\mathrm{IRM}}(T,t)=M_{\mathrm{IRM}}(T,0)-S(T)\ln(1+t)$.

romagnetic in character. With the increase in $H_{\mathrm{dc}}$ the reduction in $\chi''(T)$ is attributed to the inability of the domain walls to respond to the low-amplitude ac magnetic field in the presence of $H_{\mathrm{dc}}$.

Figure 6 shows the field dependence of magnetization of $Ho_5(Si_{0.8}Ge_{0.2})_4$ measured at $T=2$ K. The lower inset displays the $M(H)$ data for increasing field and a linear fit of the high-field data. We note that associated with the domain-wall motion the magnetization shows a rapid increase up to ~12 kOe. With a further increase in field the magnetization increases rather slowly and its behavior with field becomes nearly linear for fields higher than 40 kOe. At 2 K and $H=70$ kOe the magnetization is $7.6\mu_B/Ho^{3+}$, which is considerably lower than the expected saturation moment of $10\mu_B/Ho^{3+}$. It is well known that the nonsaturation tendency in magnetization is either observed in materials with a large magnetocrystalline anisotropy or in compounds with strong antiferromagnetic correlations. Magnetic materials with a large magnetocrystalline anisotropy usually also have a considerable hysteresis.[21] $Ho_5(Si_{0.8}Ge_{0.2})_4$ does not exhibit a particularly large hysteresis (at 2 K the remanent magnetization and coercive field are $1.04\mu_B/Ho^{3+}$ and 1.6 kOe, respectively, see upper inset of Fig. 6), hence the nonsaturated magnetization is a result of a noncollinear magnetic structure. From the linear extrapolation of the high-field $M(H)$ data at 2 K, the average spontaneous moment of $5.8\mu_B/Ho^{3+}$ is consistent with a canted magnetic structure with strong antiferromagnetic component, which agrees with the neutron-diffraction studies of $Ho_5(Si_{1-x}Ge_x)_4$ compounds.[25]

As described above, the magnetization of $Ho_5(Si_{0.8}Ge_{0.2})_4$ indicates the presence of both ferromagnetic and antiferromagnetic correlations, and the thermomagnetic irreversibility and the path dependence of magnetization of $Ho_5(Si_{0.8}Ge_{0.2})_4$ are likely due to frustrations of the spin system arising from these competing interactions. To probe the stability of the zero-field magnetic state we carried out relaxation measurements and the results are shown in Fig. 7. The isothermal remanent magnetization ($M_{\mathrm{IRM}}$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ exhibits a strong time ($t$) dependence, and even after 240 min there is no tendency toward saturation. The $M_{\mathrm{IRM}}$ isotherms follow logarithmic time dependence,

$$M_{\mathrm{IRM}}(T,t) = M_{\mathrm{IRM}}(T,0) - S(T)\ln(1+t), \qquad (1)$$

where $M_{\mathrm{IRM}}(T,0)$ and $S(T)$ are initial zero-field remanent magnetization and magnetic viscosity, respectively. The logarithmic time dependence of the isothermal remanent magnetization is observed in magnetic materials with hysteretic magnetization and/or spin glasses.[39,57–59] Generally, materials with high coercivity show a pronounced time-dependent behavior, however, if the applied field is higher than the coercive field the relaxation is attributed to spin-glass behavior.[57,58] We remind that at 2 K the coercive field for $Ho_5(Si_{0.8}Ge_{0.2})_4$ is 1.6 kOe (Fig. 6), whereas the relaxation measurements were performed after the application of 10 kOe field, which is much higher than the coercive field. Therefore, the strong relaxation effects in this case are of microscopic (spins) rather than macroscopic (domains) origin.

Although the logarithmic time dependence of isothermal remanent magnetization is a characteristic feature normally associated with spin glasses,[39,47] it has also been observed in materials with complex interactions without spin-glass freezing.[22,58] Therefore, to further check whether the relaxation is related to the formation of a spin-glass state, we have measured the ac susceptibility at 0.1, 1, 100, and 1000 Hz and the results are shown in Fig. 8. The peak positions associated with both the spin reorientation transition at $T_2=7$ K and bulk magnetic ordering at $T_C=50$ K in the $\chi'(T)$ data are frequency ($f$) independent. As the temperature is increased just above $T_2$, $\chi'(T)$ remains $f$—independent; however, a weak but, measurable $f$ dependence is observed in the $\chi'(T)$ data between ~22 K and $T_C$. Similar to $\chi'(T)$, the $\chi''(T)$ also shows peaks at $T_2$ and $T_C$, however, due to the thermal activation of the domain-wall processes,[55] the peak position associated with $T_C$ becomes $f$ dependent. Between 22 K and $T_C$, $\chi''(T)$ has a nonzero value. It is interesting to note that

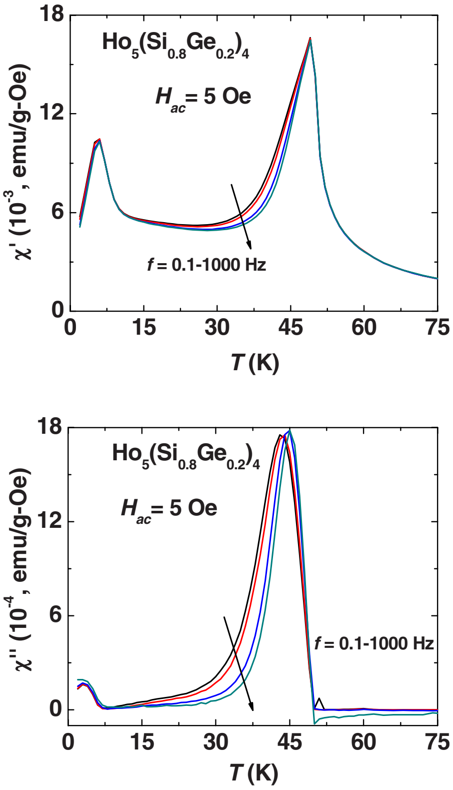

FIG. 8. (Color online) Temperature dependencies of (a) the real component ($\chi'$) and (b) the imaginary component ($\chi''$) of the ac susceptibility of $Ho_5(Si_{0.8}Ge_{0.2})_4$ measured at 0.1, 1, 100, and 1000 Hz frequencies ($f$).

the temperature (22 K) corresponding to the onset of $f$ dependence of the $\chi'(T)$ data is close to the magnetic transition occurring at $T_1$ in the $M(T)$ data (see Fig. 2). Therefore, the facts that $\chi'(T)$ is frequency dependent and $\chi''(T)$ has a nonzero value point toward the formation of a spin-glasslike state between $T_1$ and $T_C$. Even though the occurrence of the thermomagnetic irreversibility, path dependence of the magnetization, logarithmic time dependence of the isothermal remanent magnetization, and frequency dependence of ac susceptibility are hallmarks of a glassy behavior,[39,47] the latter is not expected to occur at low temperature in a perfectly ordered alloy where spins are arranged in a regular fashion in a lattice. Therefore, we choose to call this behavior “spin-glasslike.”

Magnetic frustration and randomness, or disorder [including nonmagnetic atom disorder (NMAD) (Ref. 60)], are the key ingredients for the formation of a glassy state.[47] In the lanthanide-based intermetallic compounds the long-range oscillatory nature of RKKY interactions may play a role similar to that of competing exchange interactions or a topological frustration in a conventional spin glass.[47,49] Five nonequivalent sites for the $Ho^{3+}$ ions result in considerable variations in the interatomic bond distances[18] in $Ho_5(Si_{0.8}Ge_{0.2})_4$ and quite likely lead to competing interactions originating from the oscillatory nature of RKKY exchange. Local variations in the Si/Ge concentration (see discussion on the Griffiths phase, above) and nanotwinning[17,51] may also play a role in occurrence of competing interactions due to varying exchange interactions. Furthermore, the statistical variations in the Si-Ge ratio at each Si/Ge atom site will also act as a NMAD, thereby leading to the fulfillment of the criteria for a glassy state.[47] Even though the frequency dependence of $\chi'(T)$ data indicates a glassy state in $Ho_5(Si_{0.8}Ge_{0.2})_4$, frequency independence of the peak at $T_C$, and a distinct λ-type peak in the heat capacity (see below) at $T_C$ point toward the long-range magnetic order at $T_C$. Therefore, if a glassy state is present in $Ho_5(Si_{0.8}Ge_{0.2})_4$, it coexists with the long-range ferromagnetic order. It was reported that in compounds with weak frustration and disorder, the long-range magnetic order and the glassy state may subsist.[39] Such a coexistence of long-range order and spin glass has indeed been reported in many intermetallic compounds.[61–64]

Figure 9(a) shows the temperature variation of the zero-field heat capacity ($C$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$. Adopting the method discussed by Gschneidner *et al.*,[8] the nonmagnetic, i.e., the electronic and lattice contributions to the total heat capacity of $Ho_5(Si_{0.8}Ge_{0.2})_4$ have been estimated using the prorated heat capacities of $La_5Si_4$ and $Lu_5Si_4$ [9% $La_5Si_4$ and 91% $Lu_5Si_4$]. The magnetic heat capacity ($C_{mag}$) obtained by subtracting the nonmagnetic contribution is shown in Fig. 9(b). Associated with the bulk magnetic ordering, the zero field $C(T)$ shows a λ-type peak at 49 K, which is close to the $T_C$ determined from the $M(T)$ data. The λ-type anomaly in the $C(T)$ near $T_C$ indicates that the ordering process has a second-order character. Apart from the peak at $T_C$, the spin reorientation occurring at $T_1$=23 K is reflected by a weak anomaly in the $C(T)$. It may be noted that the $C(T)$ data also exhibit an anomaly at ~16 K, which is consistent with the previous reports[23,37,38] on other $Ho_5(Si_{1-x}Ge_x)_4$ alloys. The presence of this additional anomaly at 16 K is likely the reason for the broad nature of the magnetic transition at $T_1$ in the $M(T)$ data (see Fig. 2). No signature of the magnetic transition associated with spin reorientation at $T_2$=7 K could be found in the $C(T)$ data.

The anomalies associated with the spin reorientation transitions and the bulk magnetic ordering are more clearly seen in the temperature variation in $C_{mag}$ [see Fig. 9(b)]. At low temperatures $C_{mag}$ increases rapidly with temperature and peaks around 16 K. With further increase in temperature the $C_{mag}$ increases rather slowly and exhibits another peak at $T_1$=23 K. Between $T_1$ and $T_C$, the $C_{mag}$ remains almost constant and a sudden drop in $C_{mag}$ is seen at $T_C$. Above $T_C$, the $C_{mag}$ decreases monotonically with increasing temperature.

Using the temperature dependence of $C_{mag}$ we have also determined the temperature variation in magnetic entropy ($S_{mag}$) and the results are shown as an inset of Fig. 9(b). The experimental value of the total magnetic entropy for $Ho_5(Si_{0.8}Ge_{0.2})_4$ is 122 J mol$^{-1}$ K$^{-1}$, which compares well with the expected magnetic entropy, i.e., the $R\ln(2J+1)$ value of 118 J mol$^{-1}$ K$^{-1}$. At $T_C$ the magnetic entropy is 78% of the maximum value and the full magnetic entropy is released well above $T_C$. It is well known that in intermetallic compounds containing rare earth other than Gd, a certain part of the $S_{mag}$ is tied up with crystal-field effects.[65] Furthermore, the presence of short-range magnetic correlations[66] and/or spin fluctuations[67] shifts the magnetic entropy to temperatures above the ordering temperature. Therefore, at $T_C$ the nonsaturation of $S_{mag}$ in the present case may be attrib-

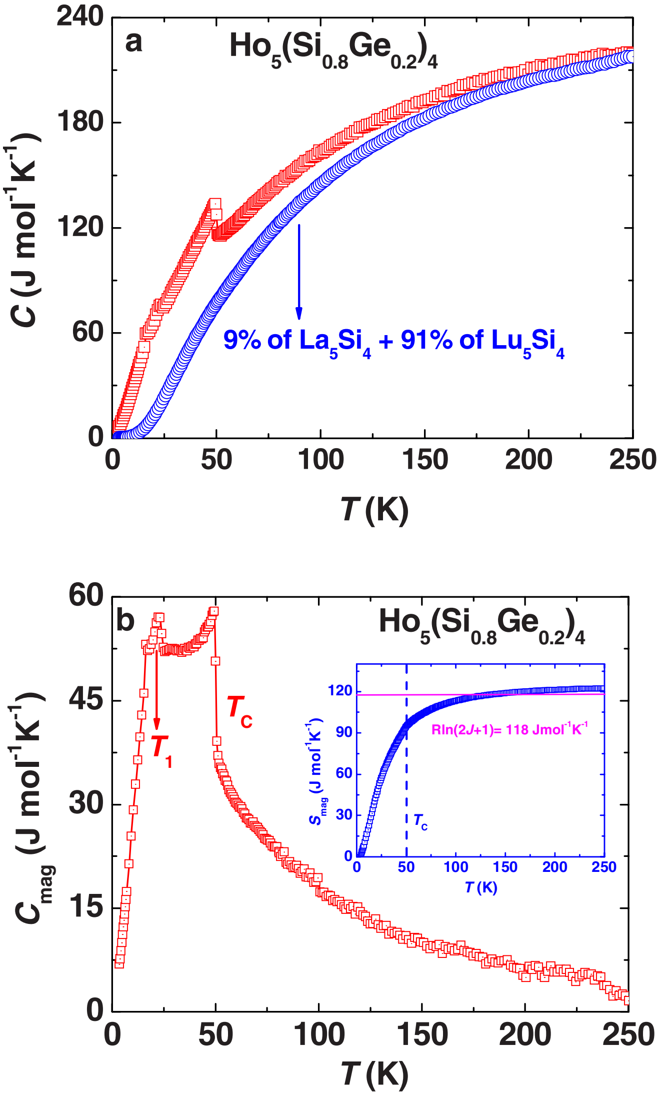

FIG. 9. (Color online) (a) Temperature dependence of the zero-field total heat capacity ($C$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ along with the prorated heat capacities of $La_5Si_4$ and $Lu_5Si_4$ to mimic the nonmagnetic contribution to the heat capacity; and (b) temperature variation in the magnetic part of the heat capacity ($C_{mag}$). The inset in (b) shows the temperature dependence of magnetic entropy ($S_{mag}$); the theoretical magnetic entropy is also given.

uted to crystal-field effects and/or short-range magnetic clustering arising from the Griffiths-type phase and/or spin fluctuations discussed above.

The MCE of $Ho_5(Si_{0.8}Ge_{0.2})_4$ has been determined both in terms of the isothermal magnetic entropy change ($\Delta S_M$, in volumetric units using the x-ray density of 7.916 g/cm$^3$) and the adiabatic temperature change ($\Delta T_{ad}$), see Fig. 10. The MCE of $Ho_5(Si_{0.8}Ge_{0.2})_4$ shows a peak near $T_C$. The maximum values of $\Delta S_M$ ($\Delta S_M^{max}$) and $\Delta T_{ad}$ ($\Delta T_{ad}^{max}$) obtained for various field changes ($\Delta H$) are given in Table II. The values for $\Delta H$=50 kOe have been obtained assuming a $H^{2/3}$ dependence of $\Delta S_M$ and $\Delta T_{ad}$. For $\Delta H$=50 kOe, the $\Delta S_M^{max}$ of other materials such as (Dy,Er)$Al_2$ compounds with $T_C$ between 50 and 100 K lies between ~60 and 110 mJ cm$^{-3}$ K$^{-1}$, whereas the $\Delta T_{ad}^{max}$ varies between 7 and 11 K.[5,68] For the same field change, the $\Delta S_M^{max}$ and $\Delta T_{ad}^{max}$ of $Ho_5(Si_{0.8}Ge_{0.2})_4$ are 78 mJ cm$^{-3}$ K$^{-1}$ and 3.9 K, respectively. Therefore, $Ho_5(Si_{0.8}Ge_{0.2})_4$ may be a potential candidate for refrigeration applications around 50 K. As follows from Fig. 10, the MCE is also significant between $T_1$=23 K and $T_C$. Considerable MCE between $T_1$ and $T_C$ indicates that significant magnetic entropy is associated with the magnetic transition at $T_1$, which corroborates with the heat capacity data [see Fig. 9(b)].

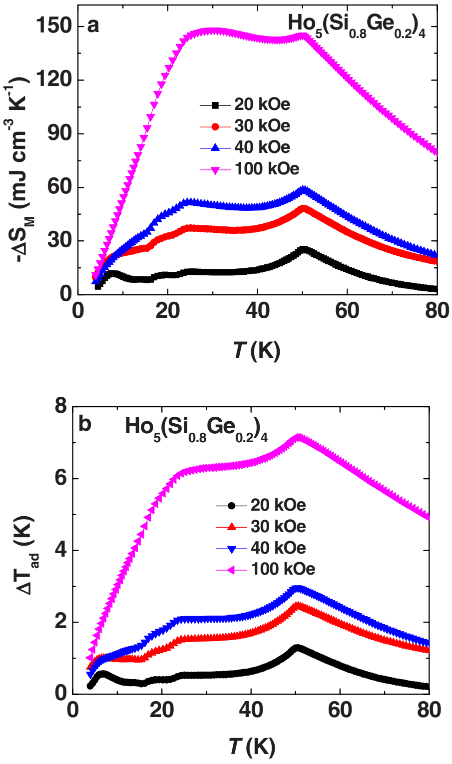

FIG. 10. (Color online) Temperature dependencies of isothermal magnetic entropy change ($\Delta S_M$) and adiabatic temperature change ($\Delta T_{ad}$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ obtained for various field changes ($\Delta H$).

Apart from $\Delta S_M^{max}$ and $\Delta T_{ad}^{max}$ magnetic refrigerant materials may be characterized by their relative cooling power (RCP). The RCP is a measure of the heat transfer between the cold and hot sinks in an ideal refrigeration cycle and can

TABLE II. The maximum values of the isothermal magnetic entropy change ($\Delta S_M^{max}$), the relative cooling power (RCP), and the maximum adiabatic temperature change ($\Delta T_{ad}^{max}$) of $Ho_5(Si_{0.8}Ge_{0.2})_4$ at ~50 K obtained for various field changes ($\Delta H$).

| $\Delta S_M^{max}$ (mJ/cm$^3$ K) | RCP (J/cm$^3$) | $\Delta T_{ad}^{max}$ (K) | $\Delta H$ (kOe) |
|---|---|---|---|
| 25 | 0.7 | 1.3 | 20 |
| 48 | 2.8 | 2.5 | 30 |
| 59 | 3.5 | 3 | 40 |
| 78[a] | 5.0[a] | 3.9[a] | 50[a] |
| 145 | 10.4 | 7.2 | 100 |

[a] The values have been estimated from the $H^{2/3}$ ($H$=magnetic field) dependence of the magnetocaloric properties.

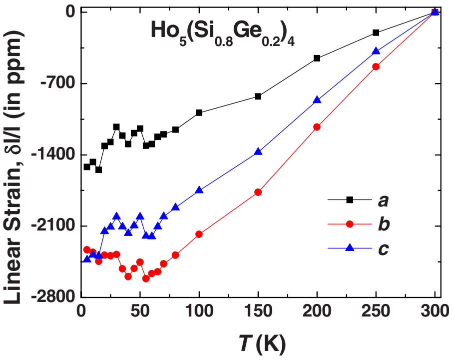

FIG. 11. (Color online) Temperature dependencies of linear thermal strain as determined from x-ray data collected during cooling from 300 to 5 K.

be defined as the product of $\Delta S_M^{\max}$ and the full width at half maximum of the $\Delta S_M$ vs $T$ plot.[5] For $\Delta H = 50$ kOe the RCP of Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ is 5 J cm$^{-3}$, whereas for the same field change the RCP of DyAl$_2$ and GdAl$_2$ is ~3 J cm$^{-3}$ and 2 J cm$^{-3}$, respectively.[5] Despite of the comparable $\Delta S_M^{\max}$, the relative cooling power of Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ is higher than those of *R*Al$_2$ compounds. The large value of RCP of Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ originates from considerable MCE existing over an extended temperature range. The nearly constant $\Delta T_{ad}$ value from 20 to 70 K [see Fig. 10(b)] makes the title compound a nearly ideal magnetic refrigerant for an Ericsson thermodynamic refrigeration cycle, which requires that $\Delta T_{ad}$ be a constant over the temperature span between the hot and cold ends of the magnetic regenerator.[5]

### B. Low-temperature x-ray diffraction studies

In view of the strong coupling between the magnetic and crystallographic sublattices of many of the $R_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds,[18] we have carried out the temperature-dependent x-ray diffraction studies over the temperature span of 5–300 K. The x-ray diffraction experiments reveal that the Gd$_5$Si$_2$Ge$_2$-type monoclinic structure of Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ is preserved down to 5 K. In contrast, other $R_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds (where $R$=Gd, Tb, and Dy), which also crystallize in the monoclinic structure at room temperature, exhibit magnetostructural transitions (MST),[18,20,21] and therefore, the absence of the same in Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ is quite unusual.

Using the lattice parameters determined from the x-ray data measured during cooling from 300 to 5 K, the temperature dependencies of the linear thermal strain are shown in Fig. 11. Along each of the three independent axes, the thermal strain varies nearly linearly above 75 K, and the strains associated with the magnetic ordering at $T_C$ show distinct anomalies. The coefficients of linear thermal expansion ($\alpha$) along *a*, *b*, and *c* axes are $0.529 \times 10^{-5}$ K$^{-1}$, 1.10 $\times 10^{-5}$ K$^{-1}$, and $0.889 \times 10^{-5}$ K$^{-1}$, respectively. These values compare well with the coefficients of linear thermal expansion reported for Gd$_5$Ge$_4$.[15,69] The coefficient of volumetric thermal expansion $[\alpha_V = (dV/dT)/V]$ is $2.6 \times 10^{-5}$ K$^{-1}$ and is also comparable to the $\alpha_V$ of Gd$_5$Ge$_4$.[15]

Apart from $T_C$, a distinct anomaly in linear thermal strain is also observed at $T_1$. It is well known that magnetostriction is associated with spontaneous changes in the long-range magnetic ordering of magnetic materials.[70] Therefore, the anomaly at $T_1$ clearly indicates that the magnetic transition at $T_1$ does not originate from a spin-glass transition, which corroborates the occurrence of a distinct anomaly in the heat-capacity data (see Fig. 9).

### C. Theoretical investigations

The experimental investigations described above clearly establish that although the Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ crystallizes in the Gd$_5$Si$_2$Ge$_2$-type (M-type) structure at room temperature, it does not exhibit a MST. Thus, in order to gain insight into the magnetostructural properties of the $R_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds in general, we have employed the tight-binding linear muffin-tin orbital method (TB-LMTO) within the framework of the local spin-density approximation (LSDA) to calculate the exchange energy corresponding to the M-type and O-I-type structures for Gd$_5$(Si$_{0.5}$Ge$_{0.5}$)$_4$, Tb$_5$(Si$_{0.55}$Ge$_{0.45}$)$_4$, Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$, and Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ compounds. For the calculations, the atomic positions and lattice constants for Gd$_5$(Si$_{0.5}$Ge$_{0.5}$)$_4$ were taken from Ref. 53, and for Tb$_5$(Si$_{0.55}$Ge$_{0.45}$)$_4$ and Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$ the parameters were taken from Refs. 71 and 21, respectively. In order to estimate the lattice constants for the hypothetical O-I structure of Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$, we plotted (not shown here) the lattice constants of the O-I polymorphs of Gd$_5$(Si$_{0.5}$Ge$_{0.5}$)$_4$, Tb$_5$(Si$_{0.55}$Ge$_{0.45}$)$_4$, and Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$ as a function of weighed atomic radius, and the lattice constants for O-I Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ ($a$=7.3361 Å, $b$=14.4727 Å, and $c$ =7.6359 Å) were determined by a linear fit of these data. Since Dy and Ho are adjacent to each other in the periodic table, and the ratios of Si and Ge in Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$ and Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$ are close to one another, the atomic positions for the hypothetical O-I polymorph of the Ho compound were taken as those of the O-I polymorph of Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$.

The exchange energies corresponding to M and O-I polymorphs of Gd$_5$(Si$_{0.5}$Ge$_{0.5}$)$_4$, Tb$_5$(Si$_{0.55}$Ge$_{0.45}$)$_4$, Dy$_5$(Si$_{0.75}$Ge$_{0.25}$)$_4$, and Ho$_5$(Si$_{0.8}$Ge$_{0.2}$)$_4$, were calculated from the spin-polarized total-energy calculations. The first-principles calculations have been performed using the semi-relativistic (including mass velocity and Darwin correction) version of the TB-LMTO (Ref. 72) method within the framework of the LSDA.[73] The 4*f* electrons of rare earth atoms were treated as core electrons so that each *R* atom has three electrons entering into the valence bands. The number of 4*f* electrons in the fractional core is fixed to an integer, and the spin and orbital 4*f* moments are described by the well known Russell-Saunders coupling scheme. This treatment of the 4*f* electrons corresponds to the accepted $R^{3+}$ state for the *R* atoms in compounds formed. In these calculations, a total of 125 and 170 irreducible **k** points have been used from the $8 \times 8 \times 8$ Brillouin-zone mesh for **k**-space integration in the O-I and M-type phases, respectively.

Since the 4*f* magnetic moments of *R* atoms are localized, the Heisenberg-type Hamiltonian for the dependence of energy on spin configuration may be applied to lanthanide based systems assuming indirect RKKY-type exchange inter-

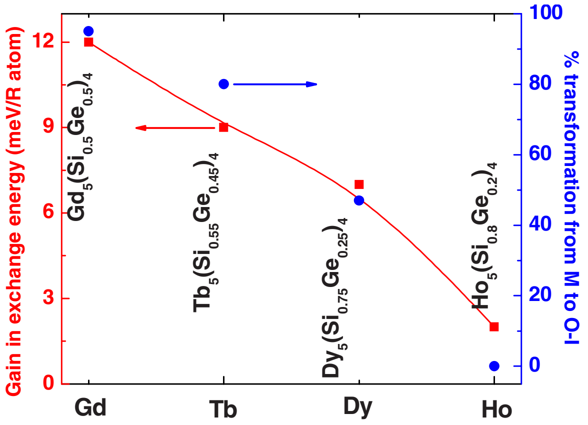

FIG. 12. (Color online) Schematic variation in the gain in the magnetic exchange energy (filled squares) involved in the $Gd_5Si_2Ge_2$-type monoclinic (M-type) to $Gd_5Si_4$-type orthorhombic (O-I) transformation and the amount of the M to O-I transformation (filled circles) in various $R_5(Si_{1-x}Ge_x)_4$ compounds.

actions via conduction electrons. The spin Hamiltonian with zero external magnetic field is given by[74]

$$H = -\sum_{i}\sum_{\delta} J_{i,i+\delta}\vec{S}_i\vec{S}_{i+\delta}, \qquad (2)$$

where $J_{i,i+\delta}$ is an exchange-coupling constant ($J$) between the spin $\vec{S}_i$ and its nearest-neighbor spin $\vec{S}_{i+\delta}$ separated by $\delta$. Since these $R_5(Si_{1-x}Ge_x)_4$ compounds are layered (slab) compounds, the exchange-coupling energy may be defined as the energy required to align moment-carrying neighboring slabs ferromagnetically,[75] i.e., $J_0 = E_{AFM} - E_{FM}$. This means that instead of considering nearest-neighbor atomic spin Heisenberg model, here we consider the nearest-neighbor slabs model, which is observed experimentally in these systems.[76]

Figure 12 shows the gain in the exchange energy ($\Delta E_e$) brought about by the M to O-I transformations in $Gd_5(Si_{0.5}Ge_{0.5})_4$, $Tb_5(Si_{0.55}Ge_{0.45})_4$, $Dy_5(Si_{0.75}Ge_{0.25})_4$, and $Ho_5(Si_{0.8}Ge_{0.2})_4$ compounds. We recall that although the $Gd_5(Si_{0.5}Ge_{0.5})_4$ exhibits a nearly complete (~93%) transformation from M to O-I structure, the degree of conversion decreases as the Gd is replaced by other heavy lanthanides. The percentage of the M to O-I transformation for various $R_5(Si_{1-x}Ge_x)_4$ compounds is also shown in Fig. 12. The enhancement in the exchange energy caused by the M to O-I conversion in $Gd_5(Si_{0.5}Ge_{0.5})_4$ is 12 meV/Gd whereas in the case $Tb_5(Si_{0.55}Ge_{0.45})_4$, $Dy_5(Si_{0.75}Ge_{0.25})_4$, and $Ho_5(Si_{0.8}Ge_{0.2})_4$ compounds, $\Delta E_e$ is 9 meV/$R$, 7 meV/$R$, and 2 meV/$R$, respectively. It is clear that the degree of completeness of the M-type to O-I transformation follows the variations seen in $\Delta E_e$. In magnetic materials involving MST, the completion of the structural transition is determined by the balance between the magnetic energy and the strain energy.[77,78] Since the volume discontinuities associated with M to O-I transition are similar in $Gd_5(Si_{0.5}Ge_{0.5})_4$, $Tb_5(Si_{0.55}Ge_{0.45})_4$, and $Dy_5(Si_{0.75}Ge_{0.25})_4$,[18,20,21] the contribution from the strain energy in these compounds is also expected to be similar. Therefore, the completeness of the structural transitions in compounds with $R$=Tb and Dy would require approximately the same gain in magnetic energy as in $Gd_5(Si_{0.5}Ge_{0.5})_4$. However, $\Delta E_e$ is reduced as $R$ is changed from Gd to other heavy lanthanides (see Fig. 12) and, thus, for the compounds with $R$=Tb and Dy the gain in the magnetic energy becomes insufficient to compensate for the strain energy, thereby leading to the incomplete structural transitions in these compounds. Thus, we believe that the absence of the M to O-I MST in $Ho_5(Si_{0.8}Ge_{0.2})_4$ is also a consequence of low $\Delta E_e$.

## IV. SUMMARY AND CONCLUSIONS

The magnetization, heat-capacity, and temperature-dependent x-ray diffraction data reveal that despite of crystallizing in the $Gd_5Si_2Ge_2$-type monoclinic structure at room temperature $Ho_5(Si_{0.8}Ge_{0.2})_4$ does not exhibit any magnetostructural transition and the monoclinic structure is preserved down to 5 K. The compound orders ferromagnetically at 50 K, and it exhibits the signature of the Griffiths phase at temperatures well above $T_C$. In $Ho_5(Si_{0.8}Ge_{0.2})_4$, the magnetization, heat capacity and linear thermal strain clearly indicate long-range magnetic order; however, the logarithmic variation in the time dependence of magnetization and frequency dependence of the ac susceptibility point toward the presence of a spin-glasslike state below $T_C$. The spin-glasslike feature in the title compound is a consequence of competing interactions originating from the long-range oscillatory nature of RKKY interactions, the compositional variations at the nanoscale, and disorder arising from the short-range variations in the Si-Ge ratio. The first-principles calculations show that in $R_5(Si_{1-x}Ge_x)_4$ compounds the gain in exchange energy brought about by the M to O-I transformation decreases as $R$ is changed from Gd to Tb, Dy, and Ho. This lowering in the gain of exchange energy is responsible both for the incompleteness of the structural transitions in $Tb_5(Si_{0.55}Ge_{0.45})_4$ and $Dy_5(Si_{0.75}Ge_{0.25})_4$, and for the absence of the M to O-I transformation in $Ho_5(Si_{0.8}Ge_{0.2})_4$.

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