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Magnetic anomalies in $Gd_6Co_{1.67}Si_3$ and $Tb_6Co_{1.67}Si_3$

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Abstract

The compounds $Gd_6Co_{1.67}Si_3$ and $Tb_6Co_{1.67}Si_3$, recently reported to form in a $Ce_6Ni_2Si_3$-derived hexagonal structure (space group: $P6_3/m$) and to order magnetically below 295 and 190 K respectively, have been investigated by means of detailed magnetization (M) studies in the temperature interval 1.8–330 K as a function of magnetic field (H). The points of emphasis are as follows. We observe multiple steps in the $M(H)$ curve for the Tb compound at 1.8 K while increasing H, but these steps do not appear in the reverse cycle of H. At higher temperatures, such steps are absent. However, this 'staircase' behavior of $M(H)$ is not observed for the Gd compound at any temperature and the isothermal magnetization is not hysteretic, unlike the case for the Tb compound. From the $M(H)$ data measured at close intervals of temperature, we have derived the isothermal entropy change (ΔS) and it is found that ΔS follows a theoretically predicted $H^{2/3}$ dependence.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, the family of non-stoichiometric compounds $R_6Co_{1.67}Si_3$ (R = rare earth), has been reported to form [1, 2] with a hexagonal structure derived from $Ce_6Ni_2Si_3$ (space group: $P6_3/m$). The crystallographic details have been presented in great detail in the recent literature [1–5]. In this crystal structure, there are two sites for R, while Co has three sites. This structure consists of chains made up of trigonal prisms of R atoms sharing a face. It appears that there is a strain in the lattice, resulting in a small c-axis length, and the partial occupation of one of the Co sites is presumably a manifestation of this strain. In this paper, we focus our attention on Gd and Tb analogues, which have been found to order magnetically below 295 and 190 K respectively [1, 4]. This investigation is a continuation of our recent work [6] on hexagonal Gd_4Co_3, the crystal structure of which is closely related [4] to that of the family under discussion. Following initial reports on the complex magnetic behavior of these two compounds [1, 4], we considered it important to probe magnetization (M) behavior in detail as a function of temperature (T) and magnetic field (H). We find that the features in the vicinity of the onset of magnetic ordering are sensitive to initial applications of a field. The most noteworthy finding is that, at 1.8 K, there are multiple steps in the isothermal M data for the Tb compound, whereas for a marginal increase of temperature, such a staircase-like behavior is absent; also, the Gd compound does not show such an anomaly. Since we measured isothermal M at several temperatures, we have also looked at the magnetocaloric effect (MCE), considering current interest in looking for materials exhibiting large MCE in different temperature ranges and looking for a relationship between MCE and H. We would like to mention that, at the time of writing this paper, we came to know of another article [5] on MCE behavior of the Gd compound, the results of which are in good agreement with ours.

2. Experimental details

The samples in polycrystalline form have been prepared by arc melting together stoichiometric amounts of high purity (>99.9 wt%) constituent elements in an atmosphere of argon. The weight loss after several meltings was negligible. The ingots were annealed at 1073 K for 1 month in an evacuated sealed quartz tube. The samples were characterized by means of x-ray diffraction (Cu Kα) and patterns revealed the

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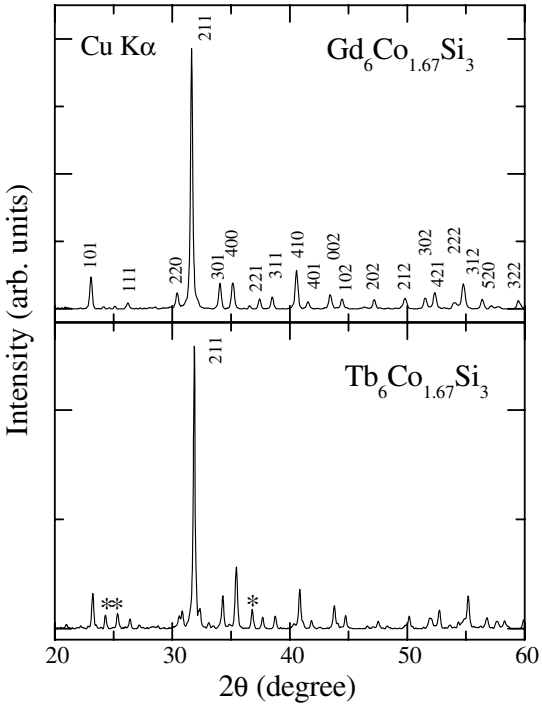

Figure 1. X-ray diffraction patterns for $Gd_6Co_{1.67}Si_3$ and $Tb_6Co_{1.67}Si_3$. Weak extra lines marked by asterisks are attributable to Tb_5Si_3.

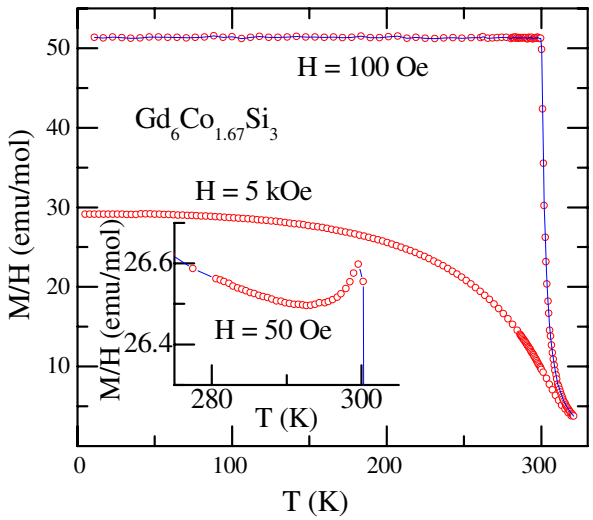

Figure 2. Magnetization divided by magnetic field as a function of temperature, measured in the presence of various fields for $Gd_6Co_{1.67}Si_3$, for the zero-field-cooled (points) and field-cooled (lines) conditions for the specimen. In the inset, the data set for $H = 50$ Oe is shown in an expanded form in the vicinity of the onset of magnetic transition for Gd sample.

formation of the compounds; for the Tb compound, however, there are a few weak extra lines (about 5% intensity) as shown by the asterisk in figure 1 attributable to Tb_5Si_3, as known from the literature [1]. The dc $M(T)$ ($T = 1.8$–300 K) behavior was measured with a commercial (Quantum Design) SQUID magnetometer in the presence of different fields for the zero-field-cooled (ZFC, from 330 K for the Gd sample, and from 250 K for the Tb sample) and field-cooled (FC) conditions for the specimens in the form of ingots; in addition, study of the isothermal M behavior at several temperatures was performed up to 70 kOe for the ZFC condition with the same instrument. For the Tb case, we have extended $M(H)$ measurements to higher fields (120 kOe) with a vibrating sample magnetometer (VSM; Oxford Instruments). In addition, for the Tb compound, we have measured the ac susceptibility (χ) with four different frequencies and an ac field of 1 Oe, to look for possible spin-glass features.

3. Results and discussion

$M(T)$ curves obtained in various fields are shown in figures 2 and 3 for these compounds. There is a distinct evidence for the onset of magnetic ordering near 300 K and 200 K for the Gd and Tb compounds respectively. It is to be noted that, for the Gd sample, the jump in the magnetization is quite sharp and there is a weak peak at the magnetic transition, if the magnetization is measured in very low fields (see the curve for $H = 50$ in the inset of figure 2). Well below the magnetic transition temperature, the value of M is nearly constant. We do not find any bifurcation of ZFC and FC curves for this compound. The feature at the transition point is sharp for the Tb sample as well at low fields (see figure 3). However, the ZFC curves bifurcate, presumably due to domain wall pinning effects, often reported (see, for instance, [7]) in the literature for materials with long-range magnetic order (but such an effect is absent for the Gd case, as inferred from the data discussed above). The bifurcation temperatures (for Tb sample) are about 180 K and 30 K for $H = 100$ Oe and 5 kOe respectively; as noted in [1], it appears that there is another feature around 20–40 K in the form of a drop in the ZFC curves. It is not clear whether this temperature range marks the onset of a highly metastable state, the magnetization of which is sensitive to the history of measurements. In order to address whether the ZFC–FC χ irreversibility for the Tb case arises from spin-glass behavior, we have performed ac χ measurements with 1.3, 13, 133 and 1333 Hz and we did not find any frequency dependence of the features, thereby ruling out spin-glass freezing in the temperature range of investigation; there are peaks near 120, 170 and 183 K, as though there is more than one magnetic transition (see figure 3 for a typical curve). There appear to be corresponding features in the ZFC curves, though broad, at 120 and 170 K for low dc fields in the dc χ data. One cannot rule out the possibility that the weak 120 K transition arises from the Tb_5Si_3 secondary phase (and possibly from traces of TbCoSi) ordering magnetically in that range [8, 9]. (On the basis of $M(H)$ data discussed below, we infer that there is an antiferromagnetic component in zero field, though the observation of hysteretic $M(H)$ behavior, however weak it may be at higher temperatures, implies that the net magnetic structure is ferrimagnetic, as inferred in [1]). With respect to paramagnetic data, we could not look for the Curie–Weiss region for the Gd sample, as the magnetic transition is near the extreme high temperature limit of our magnetization

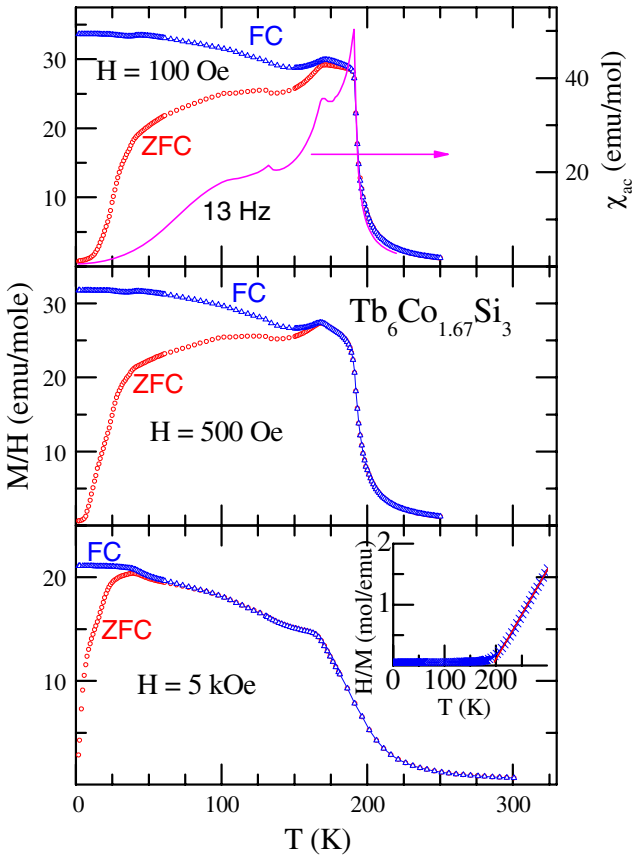

Figure 3. Magnetization divided by magnetic field as a function of temperature, measured in the presence of various fields for $Tb_6Co_{1.67}Si_3$, for the zero-field-cooled and field-cooled conditions for the specimen. The ac susceptibility data set measured with a frequency of 13 Hz is also plotted. In the inset, inverse susceptibility is plotted and a line through the Curie–Weiss region is drawn.

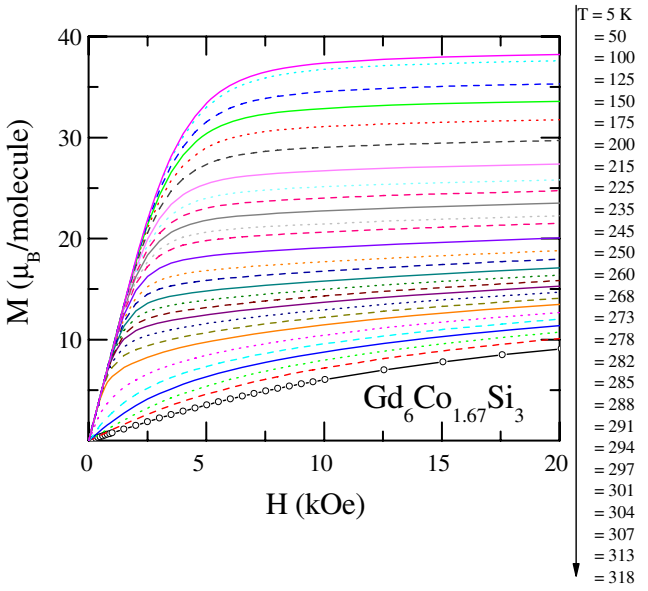

Figure 4. Isothermal magnetization behavior at several temperatures for the zero-field-cooled condition for the specimen, $Gd_6Co_{1.67}Si_3$. The curves are non-hysteretic. While for 318 K the data points are shown, for others only the lines are shown for the sake of clarity.

measurements. For the Tb sample, the magnetic susceptibility follows Curie–Weiss behavior above 205 K as shown in the inset of figure 3 and the paramagnetic Curie temperature is about 195 K; the effective moment obtained from the linear region is ∼9.62 μ_B/Tb, which is close to the value expected for free trivalent Tb ions within the limits of experimental error (0.1 μ_B).

In figure 4, we show the isothermal magnetization behavior measured at close intervals of temperature for the Gd compound. For the Gd case, there is a deviation from linearity at high fields in the paramagnetic state, attributable to short-range correlations. In the magnetically ordered state, after an initial rise (until about 5 kOe), M tends towards saturation at higher fields with a very weak gradual increase beyond 5 kOe. The curves for this compound are featureless at high fields (and hence not shown in figure 4 beyond 20 kOe). The value of the saturation moment obtained by extrapolation of the high field data to zero field is about 6.3 μ_B/Gd at 5 K, which is less than the free ion value of 7 μ_B/Gd. While [4] a higher value of about 6.8 μ_B/Gd has been reported, our value is the same as that in another recent report [10] which appeared in print after submission of this paper for publication. Therefore, we conclude that there is an induced moment on Co, coupled antiparallel to that of Gd moment and/or canted antiferromagnetism. The $M(H)$ curves are not found to be hysteretic for the Gd compound. These findings, in broad agreement with [4] and [5], imply that this compound can be classified as a soft ferrimagnet.

For the Tb sample, the curves (see figure 5) are essentially linear in the paramagnetic state (as expected). The behavior in the magnetically ordered state is complex. There is an irreversibility of $M(H)$ curves, the degree of which gradually increases with decreasing temperature as illustrated in figure 6 for 80 and 5 K. The fact that there is a hysteresis loop, however weak it may be, even at 80 K implies that there is a ferromagnetic component even at this temperature. The value of the coercive field is small (∼200 Oe), say at 80 K, and it increases with decreasing temperature, say, to about 8 kOe at 5 K. Above 20 K (in the magnetically ordered state), there is a sharp rise of M at low fields (see the curve for 80 K in figure 6) followed by a tendency towards saturation at higher fields as though there is a strong ferromagnetic component. Below 20 K, in the zero-field (virgin) state, there is a knee near zero field (see the 5 K curve in figure 6). The possible presence of an antiferromagnetic component at all temperatures is supported by a weak gradual increase of M even at high fields (see figure 5) without any evidence for saturation. The value of the extrapolated saturation moment (5 μ_B/Tb) at 1.8 K, obtained by linear extrapolation of the high field data to zero field, is much less than that for fully degenerate trivalent Tb ions (9 μ_B). Although, for Tb, the crystal field effect also contributes to a reduction of the saturation moment, considering the similarities with the Gd compound, we believe that a part of the reduction in extrapolated saturation moment is attributable to an antiferromagnetic component. It therefore appears that these compounds may be described as ferrimagnets. Careful neutron diffraction studies (which are

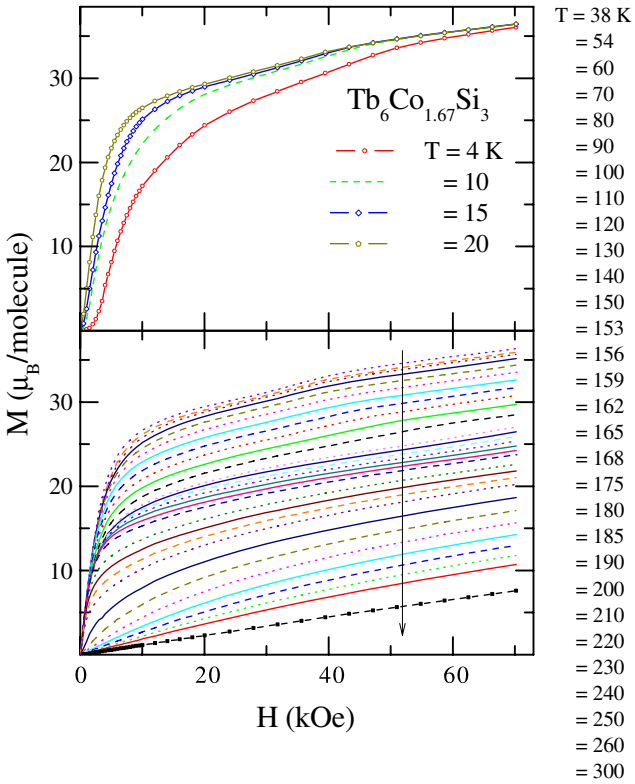

Figure 5. Isothermal magnetization behavior (virgin curves) at several temperatures for the zero-field-cooled condition for the specimens, $Tb_6Co_{1.67}Si_3$, while increasing the field. The temperatures mentioned outside the figure are for the bottom portion of the figure.

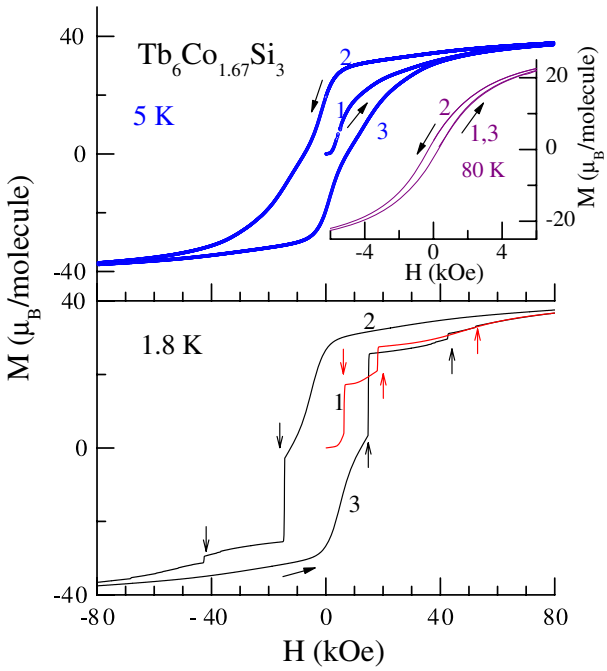

Figure 6. Magnetic hysteresis loops for $Tb_6Co_{1.67}Si_3$ at 1.8, 5, and 80 K for the zero-field-cooled condition for the specimen measured with a vibrating sample magnetometer in the field-sweep mode. Vertical arrows for $T = 1.8$ K mark the magnetic fields at which discontinuous changes in magnetization are observed. Other arrows and numbers (1, 2, 3) placed near the curves show the direction in which the field is changed.

possible for the Tb compound) are urgently warranted, to explain the complex magnetic structure.

The most fascinating finding which we are stressing in this paper is that there are multiple steps in the $M(H)$ curve at 1.8 K for the Tb sample: if the sample is cooled very fast (within a few minutes) from 300 to 1.8 K, there are three steps (near 6.2, 17.8, and 52 kOe for the specimen employed here) in the virgin curve in the data collected with VSM with a field-sweep rate of 4 kOe min^{-1} (figure 6). These steps do not appear when the field is reversed to zero, which we attribute to a 'supercooling' effect resulting in a phase-coexistence phenomenon at zero field after this field cycling, as discussed in detail, for instance, for Gd_5Ge_4 [11] and Nd_7Rh_3 [12]. Further experiments are required, however, to establish whether such a supercooling arises from magnetostructural effects or whether is purely magnetic in origin. If the current to the magnet is reversed, two steps appear, at -14.2 and -42.5 kOe. These steps vanish in the forward cycle when the field is reduced towards zero, but when the field enters the positive quadrant, these reappear at 14.5 and 42.5 kOe. Interestingly, the transition field values are found to be marginally specimen dependent, which we believe arises from partial occupancy of one of the Co sites, thereby resulting in local environmental effects. We have also noted that, if the cooling rate is slow, these transitions in the virgin curve tend to broaden, similar to what is seen for Nd_7Rh_3 [12]. In addition, we have probed the behavior of these steps by means of measurements with the SQUID magnetometer and we find that the transitions occur at marginally higher fields (shifted by about 5 kOe) as compared to those obtained with VSM. The SQUID magnetometer measures magnetization after the stabilizing of the field at a particular value (that is, for the field-stable mode rather than the field-sweep mode). Thus, it appears that the experimental conditions have a profound influence on these transitions in $M(H)$. Thus, this compound exhibits interesting multiple metamagnetic transitions at 1.8 K. The hysteresis behavior at 1.8 K is distinctly different from that at a marginally higher temperature, say 5 K, and the irreversibility is observed even at fields as high as 80 kOe. There is a knee in the virgin curve in the $M(H)$ curve, say, below 5 K, at low fields, which we attribute to the gradual dominance of an antiferromagnetic component and associated field-induced spin reorientation effects, with decreasing temperature.

We have derived information about the MCE behavior from the isothermal M data, employing its relationship with the isothermal entropy change (ΔS) through Maxwell's equation [13]. The results for ΔS thus obtained are shown in figures 7 and 8 for a variation of the field from zero to a desired value. The values are maximum at the respective magnetic ordering temperatures. Since the magnetic ordering sets in near 300 K for the Gd compound, it is quite tempting to compare the value with that for Gd for potential applications, particularly noting that the isothermal magnetization curves are not hysteretic for the Gd compound—a strongly desired factor for applications [14]. The value, say for $H = 0$ to 50 kOe, at the peak is close to half (about -6.5 J mol^{-1} K^{-1}

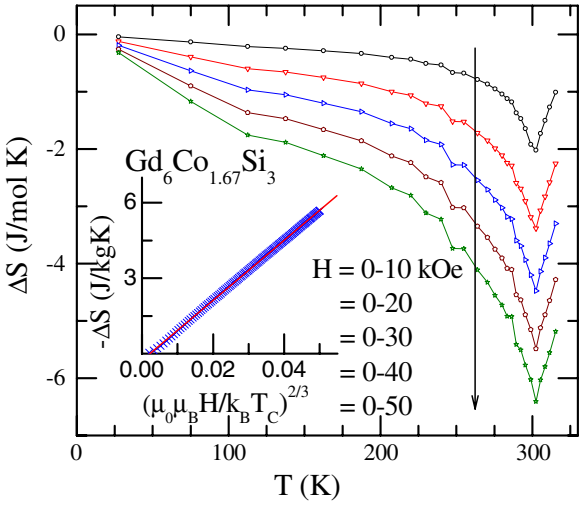

Figure 7. Isothermal entropy change (a measure of the magnetocaloric effect) for selected final magnetic fields (from the initial field of 0 Oe) as a function of temperature for $Gd_6Co_{1.67}Si_3$. A line is drawn through the data points and a vertical line is drawn to show the curves corresponding to final fields. In the inset, the same data set (in different units) is plotted to show a functional dependence on magnetic field as described in the text and the line shows the linear region.

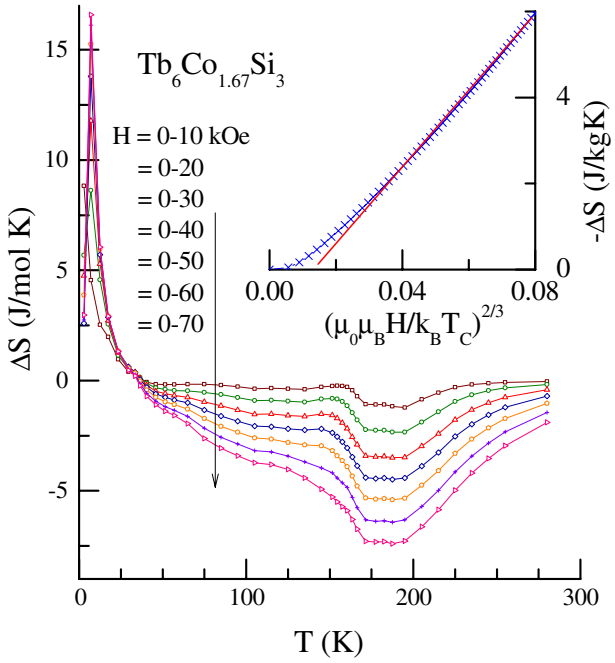

Figure 8. Magnetocaloric data for $Tb_6Co_{1.67}Si_3$ as in the caption of figure 7.

or -42 mJ cm^{-3} K^{-1}) of that for Gd metal (-77 mJ cm^{-3} K^{-1} [13]). For the Tb sample, the value at the peak is about -5.4 J mol^{-1} K^{-1} (in other words, -37 mJ cm^{-3} K^{-1}), which is much lower compared to that (-210 mJ cm^{-3} K^{-1}) for $LaFe_{11.7}Si_{1.3}$ ordering magnetically at nearly the same temperature. The refrigeration capacity (RC), defined as in [13], is found to be about 62 and 70 mJ cm^{-3} kOe^{-1} for the Gd and Tb compounds respectively, and these values are not negligible, considering that the corresponding values [13] for Gd metal and $LaFe_{11.7}Si_{1.3}$ are 110 and 93 mJ cm^{-3} kOe^{-1}. Our results for the Gd compound agree quite well with [10], which appeared in print after this paper was communicated for publication. The negative sign of ΔS implies [13] that there is a dominating ferromagnetic component at high fields, at least above 20 K. However, there is a sign reversal in the ΔS data for the Tb sample below 20 K with a significant magnitude at lower temperatures, the origin of which is not clear; possibly, this arises from a dominating antiferromagnetic component (arising from ferrimagnetism) persisting even at high fields and/or small thermal/field-cycling effects below this temperature can possibly have a profound effect on the M data at low temperatures. It is also known that ΔS derived from magnetization in a non-equilibrium state [15] may not be reliable and it is possible that this temperature marks the onset of such a non-equilibrium state.

It is now recognized theoretically [16, 17] that there is a relationship between ΔS and H. For instance, for magnetic materials with a second-order phase transition [17], $\Delta S = -kM_s(0)h^{2/3} - S(0,0)$, where h is the reduced field (given by $\mu_0\mu_B H/k_B T_C$). k is a constant and $M_s(0)$ is the saturation magnetization at low temperatures. The ΔS data for many materials were fitted to this equation successfully, but the value of $S(0,0)$ ranges from -0.2 to -1.06 kg^{-1} K^{-1}, the physical significance of which is not yet clear. We have therefore analyzed the peak value of ΔS as a function of $h^{2/3}$ and plotted this in the insets of figures 7 and 8. To enable a straightforward comparison with [17], in the insets, we present ΔS in units of J kg^{-1} K^{-1}. It is found that there is a small deviation at low h values for the Tb case as in [17], but the plot is exceptionally linear for the Gd compound. The values of $S(0,0)$ and the coefficient of the $h^{2/3}$ term for the Gd (Tb) compound are found to be -0.3 (-1.25) and -120(-90) J kg^{-1} K^{-1}, very close to the values reported in table 1 of [13]. The corresponding values of k are about 0.6 and 0.46 respectively.

4. Summary

The magnetization behavior of the compounds $Gd_6Co_{1.67}Si_3$ and $Tb_6Co_{1.67}Si_3$, ordering magnetically below about 300 and 190 K, has been systematically studied. The magnetic behaviors of these two compounds are found to be qualitatively different. The most notable of all the findings reported here is that, while increasing the magnetic field, we observe multiple steps in the isothermal magnetization for the Tb sample, that too at 1.8 K only; these steps are not observed when the field is reversed to zero and therefore this finding may have some relevance to the concepts of 'supercooling' and 'phase coexistence' following first-order transitions (see, for instance, [11] and [12]). Such features are absent for the Gd compound. There is no hysteresis in the isothermal magnetization of the Gd compound, whereas, for the Tb compound, hysteresis loops are found at all temperatures, though these loops become smaller with increasing temperature. These compounds exhibit a modest magnetocaloric effect at the respective magnetic ordering

temperatures and it is found that MCE varies essentially as $H^{2/3}$, lending support to the theory of [17].

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