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Multiple magnetic transitions and the magnetocaloric effect in $Gd_{1-x}Sm_xMn_2Ge_2$ compounds

Pramod Kumar[1], Niraj K Singh[1], K G Suresh[1,3], A K Nigam[2] and S K Malik[2]

[1] Department of Physics, IIT Bombay, Mumbai 400076, India
[2] Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400005, India

E-mail: suresh@phy.iitb.ac.in

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Abstract

The magnetic and magnetocaloric properties of polycrystalline samples of $Gd_{1-x}Sm_xMn_2Ge_2$ have been studied. All the compounds except $GdMn_2Ge_2$ show re-entrant ferromagnetic behavior. Multiple magnetic transitions observed in these compounds are explained on the basis of the temperature dependences of the exchange strengths of the rare earth and Mn sublattices. The magnetocaloric effect is found to be positive at the re-entrant ferromagnetic transition, whereas it is negative at the antiferro–ferromagnetic transition. The Sm compounds are found to show a negative magnetocaloric effect at temperatures below the re-entrant ferromagnetic transition temperature. In $SmMn_2Ge_2$, the magnetic entropy change associated with the re-entrant transition is found to decrease with field, which may be attributed to the crystal-field effect as well as the increase in the intralayer antiferromagnetic component of the Mn sublattice. The maximum value of the isothermal magnetic entropy change in this series of compounds is found to decrease with increase in Sm concentration.

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

1. Introduction

The magnetocaloric effect (MCE) was discovered by Warburg in 1881, when it was fund that iron gets heated on application of a magnetic field [1]. It is the response of a magnetic solid to a changing magnetic field, which manifests itself as a change in its temperature. For a simple ferromagnet near its Curie temperature (T_C), when a magnetic field is applied the moments get aligned parallel to the magnetic field, which lowers the magnetic entropy and causes the sample to heat up. When the magnetic field is turned off, the moments tend to

[3] Author to whom any correspondence should be addressed.

randomize, thereby increasing the entropy, and the material cools down. This process has been used for achieving sub-kelvin temperatures and this technique is known as adiabatic demagnetization. Recently, this technique has been considered for magnetic refrigeration applications in sub-room-temperature and near-room-temperature regimes [2–5]. The success of this technology, to a great extent, depends on the availability of giant magnetocaloric materials. The search for such materials suitable for cooling in the sub-room-temperature and near-room-temperature regimes is essential for further improvements in this field. Materials with first-order magnetic transition are of particular interest, since they exhibit significant changes in the isothermal magnetic entropy (ΔS_M) and the adiabatic temperature change (ΔT_{ad}) at the magnetic transition temperature. Compounds showing field-induced magnetic transitions and/or structural transitions have been found to exhibit very large values of MCE, as in the case of $Gd_5Si_2Ge_2$ [6]. A giant magnetocaloric effect was also found in systems such as MnAs, $LaFe_{11.4}Si_{1.6}$ [7–10], by virtue of a first-order ferromagnetic–paramagnetic transition.

Among the rare earth (R)–transition metal intermetallics, RMn_2Ge_2 compounds have attracted a lot of attention due to their interesting magnetic and other related properties [11–22]. These compounds, in general, crystallize in the tetragonal $ThCr_2Si_2$-type structure. In this series of compounds, both R and Mn atoms possess magnetic moments and form a layered structure of Mn–Ge–R–Ge–Mn type, with the layers perpendicular to the c-axis. The interlayer and intralayer Mn–Mn exchange interactions are very sensitive to the intralayer Mn distance, leading to ferromagnetic or antiferromagnetic ordering of the Mn sublattice. In most of the RMn_2Ge_2 compounds, the intralayer Mn sublattice, in general, exhibits antiferromagnetic ordering above room temperature, while the R sublattice remains disordered. As the temperature is reduced, the R moments also order magnetically, and this causes a change in the magnetic ordering of the Mn sublattice. By virtue of the different temperature dependences of R and Mn sublattice magnetizations, some of the compounds of this series show multiple magnetic transitions, re-entrant ferromagnetism, etc. Furthermore, the compounds with rare earths such as Sm, Gd, Dy and Tb show first-order magnetic transitions (FOTs) [23]. The occurrence of FOTs is expected to result in considerable MCE.

Recently, as part of our investigations on magnetic and magnetocaloric properties, we have reported our results on $Gd_{1-x}Sm_xMn_2Si_2$ [24] and $GdMn_2Si_{2-x}Ge_x$ [25] compounds. It is known that the magnetic nature of $SmMn_2Ge_2$ and $GdMn_2Ge_2$ shows some differences on account of their lattice parameter variations [26]. Therefore, a solid solution of these two compounds, i.e. $Gd_{1-x}Sm_xMn_2Ge_2$, would be interesting from the point of magnetic properties as well as other related properties like MCE. With this aim, we have studied the effect of Sm substitution for Gd on the magnetic and magnetocaloric properties of $Gd_{1-x}Sm_xMn_2Ge_2$ with $x = 0$, 0.4, 0.6 and 1.

2. Experimental details

Polycrystalline samples of $Gd_{1-x}Sm_xMn_2Ge_2$ with $x = 0$, 0.4, 0.6 and 1 were synthesized by arc melting the constituent elements in stoichiometric proportions in a water-cooled copper hearth under high pure argon atmosphere. The purity of the starting elements was 99.9% for the rare earths and 99.99% for Mn and Ge. The ingots were melted several times to ensure homogeneity. The as-cast samples were characterized by room-temperature powder x-ray diffractograms collected using Cu Kα radiation. The temperature (T) dependence of magnetization (M) measurements, under both 'zero-field-cooled' (ZFC) and 'field-cooled' (FC) conditions were measured in a field (H) of 200 Oe, using a vibrating sample magnetometer (VSM, Oxford Instruments). Magnetization isotherms were recorded at various temperatures in the range 5–300 K and up to a maximum field of 80 kOe.

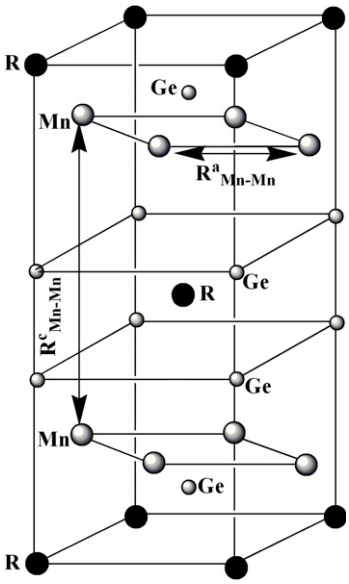

Figure 1. The unit cell of the RMn_2Ge_2 structure. Filled circles represent the rare earth sites, big shaded circles represent the transition metal sites and small shaded circles represent Ge sites.

Table 1. Lattice parameters, bond lengths and the magnetic transition temperatures in $Gd_{1-x}Sm_xMn_2Ge_2$ compounds.

x	a (Å)	c (Å)	R^a_{Mn-Mn} (Å)	R^c_{Mn-Mn} (Å)	T_1 (K)	T_2 (K)
0	4.026(1)	10.881(2)	2.847(1)	5.441(2)	96	—
0.4	4.043(1)	10.884(2)	2.859(1)	5.442(1)	85	296
0.6	4.051(1)	10.888(1)	2.864(1)	5.444(1)	84	210
1	4.062(2)	10.889(2)	2.872(2)	5.445(1)	110	146

3. Results and discussion

The Rietveld refinement of the x-ray diffractograms collected at room temperature confirms that all the compounds have formed in single phase with the $ThCr_2Si_2$ structure (space group = $I4/mmm$). The unit cell of this structure is shown in figure 1. The lattice parameters and the Mn–Mn bond lengths along the a-axis and the c-axis (i.e. R^a_{Mn-Mn} and R^c_{Mn-Mn} respectively), as obtained from the refinement, are given in table 1. It may be noticed from the table that R^a_{Mn-Mn} increases with increase in the Sm concentration, whereas R^c_{Mn-Mn} remains almost a constant. The increase in R^a_{Mn-Mn} is attributed to the larger ionic radius of Sm, compared to that of Gd. It can also be noticed that in all the compounds except $GdMn_2Ge_2$, the intralayer Mn–Mn distance (R^a_{Mn-Mn}) is greater than the critical distance of 2.85 Å, and therefore the interlayer magnetic coupling is ferromagnetic at room temperature. In the case of $GdMn_2Ge_2$, R^a_{Mn-Mn} is just below the critical distance.

Figure 2 shows the temperature variation of magnetization of $Gd_{1-x}Sm_xMn_2Ge_2$ compounds obtained in a field of 200 Oe. As can be seen, there are two transitions, one at T_1 and the other at T_2 in all the compounds, except $GdMn_2Ge_2$. In the case of $GdMn_2Ge_2$, there is only one transition at $T_1 = 96$ K. In this case, as is evident from table 1, R^a_{Mn-Mn} is slightly less than the critical distance needed for the ferromagnetic coupling of the interlayer

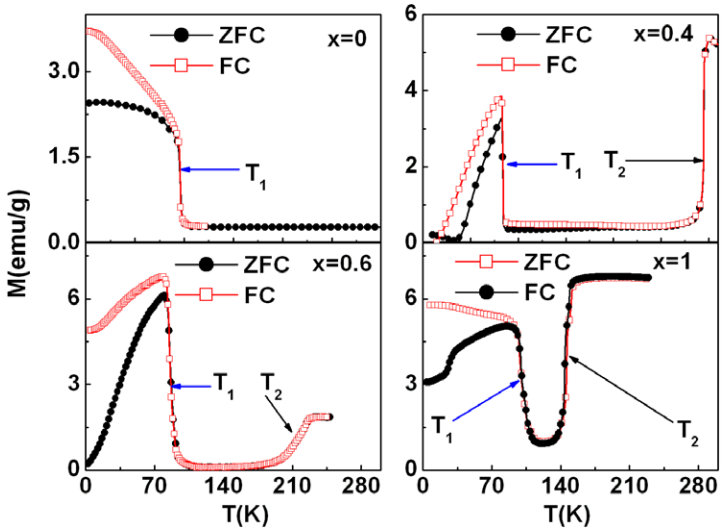

Figure 2. Temperature dependence of magnetization in $Gd_{1-x}Sm_xMn_2Ge_2$ compounds in a field of 200 Oe. The filled circles show the ZFC data and the open circles show the FC data.

Mn–Mn moments. On the other hand, the R^a_{Mn-Mn} value is just equal to the critical distance needed for non-collinear ferromagnetism within the c-plane. It is reported that $GdMn_2Ge_2$ has a Néel temperature (T_N) of 365 K [11, 12], below which the intralayer Mn–Mn coupling results in a canted magnetic structure and the interlayer coupling leads to antiferromagnetic ordering. Therefore, the overall magnetic nature of the Mn sublattice in $GdMn_2Ge_2$ is non-collinear antiferromagnetic below T_N. As a result, the net molecular field seen at the Gd site is quite small, and hence the Gd moments are disordered below T_N. As the temperature is reduced, the rare earth (Gd) ordering increases and the molecular field associated with it also increases. This results in a forced ferromagnetic state for the Mn sublattice and a net non-collinear ferrimagnetic coupling between Gd and Mn moments. This transition, which is first order in nature, occurs at $T_1 = 96$ K.

On the other hand, the scenario is quite different in $SmMn_2Ge_2$. As can be seen from table 1, the lattice parameters and the bond length R^a_{Mn-Mn} are greater than those of $GdMn_2Ge_2$. Since R^a_{Mn-Mn} is higher than the critical value, the interlayer Mn coupling leads to a canted ferromagnetic state below the ordering temperature. It has been reported that the Curie temperature of the Mn sublattice in the case of $SmMn_2Ge_2$ is about 350 K [27, 28]. As the temperature is reduced, due to the thermal contraction of R^a_{Mn-Mn}, a first-order transition from a ferromagnetic to an antiferromagnetic state within the Mn sublattice occurs at T_2. Reducing the temperature further causes the ordering of Sm moments which couple ferromagnetically with the ferromagnetic component of the Mn sublattice, which gives rise to the transition at T_1, which is also first order in nature. The ferromagnetic phase below T_1 is known as the re-entrant ferromagnetic phase [27, 28].

On substituting Sm partially for Gd, it is found that the temperature dependence of magnetization behavior is nearly the same as in $SmMn_2Ge_2$, as is evident from figure 2. It may also be noted from figure 2 that both the FC and ZFC magnetization tend to assume very low values at low temperatures. The reduction in the ZFC magnetization (with decrease in temperature) reflects the domain wall pinning effect. On the other hand, the decrease in the FC magnetization suggests that there is a tendency for compensation of the magnetization of the R

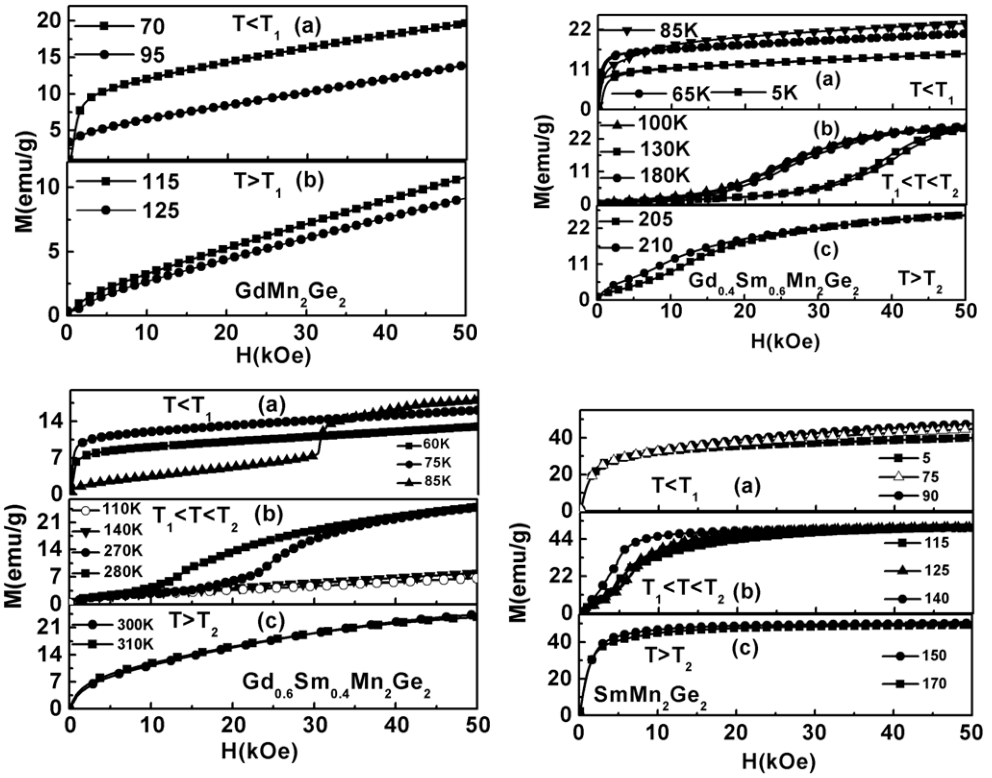

Figure 3. M–H isotherms of $Gd_{1-x}Sm_xMn_2Ge_2$ compounds at various temperatures.

and Mn sublattices. It is known that the coupling of the Mn with a light rare earth (such as Sm) is ferromagnetic, whereas the coupling with a heavy rare earth (such as Gd) is ferrimagnetic. Furthermore, the moment of Sm^{3+} is quite small compared to that of Gd^{3+}. Because of these reasons, the magnetic state in the compounds with $x = 0.4$ and 0.6 is complex.

Figure 3 shows the M–H isotherms of all the compounds at various temperatures. In the case of $GdMn_2Ge_2$, the M–H curves below T_1 reflect the ferromagnetic behavior, while those above T_1 show antiferromagnetic behavior. These observations are consistent with the M–T plots of figure 2. In comparison to $GdMn_2Ge_2$, the M–H isotherms of $SmMn_2Ge_2$ are more interesting. At temperatures below T_1, the magnetization is found to increase slightly with increase in temperature, suggesting the possibility of some antiferromagnetic component in this temperature regime. In the temperature range $T_1 < T < T_2$, the magnetization behavior indicates an antiferromagnetic nature, as expected. Furthermore, the saturation magnetization is almost insensitive to the temperature. In the case of the compound with $x = 0.4$, a metamagnetic transition from the antiferromagnetic state to a ferromagnetic state is seen below T_1 and also in the regime of $T_1 < T < T_2$. On the other hand, in the compound with $x = 0.6$, a metamagnetic transition could be observed only for $T_1 < T < T_2$. The absence of the metamagnetic transition below T_1 in this compound reflects the fact that the compound is predominantly ferromagnetic in that temperature regime. On the other hand, due to the dominant ferrimagnetic nature of the compound with $x = 0.4$, there is a metamagnetic transition below T_1 as well. Therefore, it can be seen that the M–T and M–H behavior of these compounds is consistent.

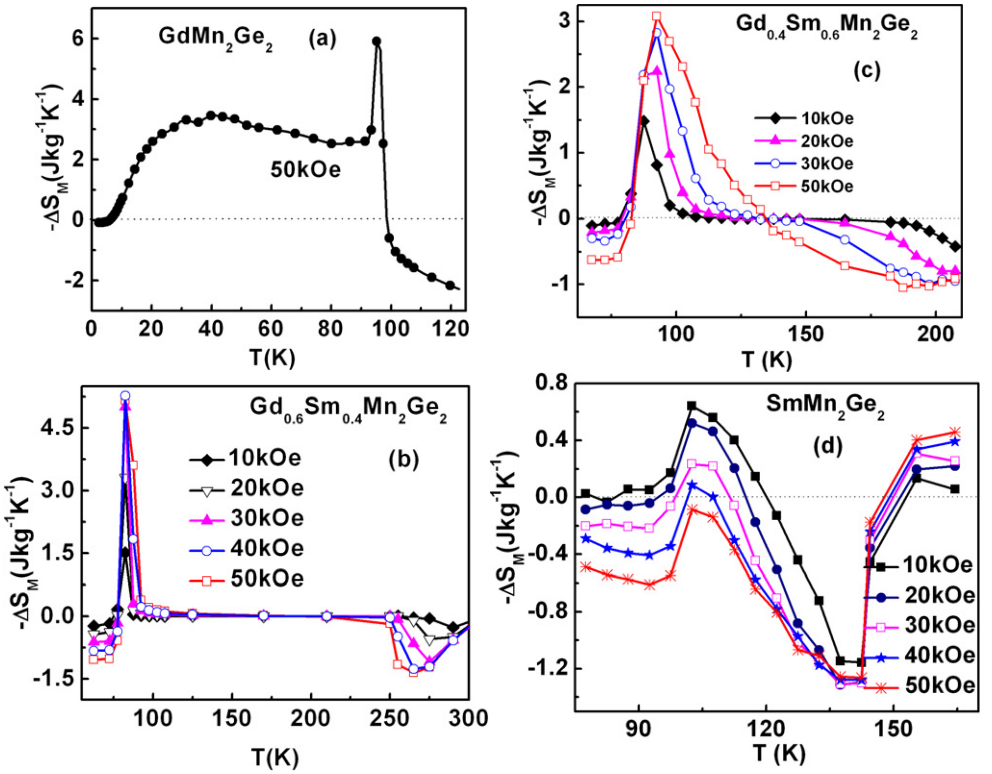

Figure 4. Temperature variation of isothermal magnetic entropy change in $Gd_{1-x}Sm_xMn_2Ge_2$ compounds in different fields.

The magnetocaloric effect in these compounds has been measured in terms of isothermal magnetic entropy change ($-\Delta S_M$) for various temperatures and applied magnetic fields, using Maxwell's equation [3, 5, 29, 30]. Figure 4 shows the temperature variation of isothermal magnetic entropy change for all the compounds, for different fields. It can be seen that, in all the compounds, the entropy change is predominantly negative (positive MCE) for the transition at T_1. Furthermore, the magnitude of the entropy change at T_1 increases with field in all the compounds, except $SmMn_2Ge_2$. The magnitude of the entropy change at T_1 is found to be the smallest in $SmMn_2Ge_2$ and also it decreases with increase in field, attaining small negative values at the highest field of 50 kOe. To the best of our knowledge, MCE studies on $SmMn_2Ge_2$ have been carried out only up to a maximum field of 10 kOe, and there are no reports of field dependence of MCE in the literature [31].

Another interesting feature common to all the Sm-containing compounds in the present series is the positive entropy change (negative MCE) at temperatures below T_1. It is of interest to note that this observation is consistent with the M–H data below T_1 obtained in these three compounds, which shows that the magnetization increases with increase in temperature. Koyama *et al* [31] have reported that the magnetic entropy change in $SmMn_2Ge_2$ for a field of 10 kOe is almost zero below 100 K. Therefore, we feel that the sign change (below T_1) observed in the present case occurs at fields greater than 10 kOe. This suggests that, below T_1, the applied field (of about 50 kOe) causes an increase in the magnetic entropy in the Sm-containing compounds. Chaudhary *et al* [28] have reported that, for fields lower than 50 kOe,

the ZFC magnetization of $SmMn_2Ge_2$ is less than the FC magnetization, for temperatures lower than T_1. However, quite strangely, the trend reverses for a field of 50 kOe. These authors have mentioned that this observation was anomalous and the origin was not clear. We feel that the present MCE variation also corroborates the observations of Chaudhary *et al*.

Barla *et al* [27] have reported that the ground state of Sm^{3+} ions in $SmMn_2Ge_2$ is $|5/2\rangle$. It is also important to note that Sm^{3+} is a special case among the trivalent lanthanides because of the considerable admixture of the excited states with the ground state. Population of the higher multiplets by the applied field would cause an increase in the entropy, thereby causing the entropy change to decrease. However, since the magnitudes of Mn and Sm moments are not very different, there may be a contribution from the Mn sublattice as well towards the anomalous magnetization and MCE behavior [32]. The noncollinear ferromagnetic structure of the Mn sublattice with significant antiferromagnetic component (intralayer) in the re-entrant phase may contribute to the positive magnetic entropy change (negative MCE).

The ΔS_M values obtained at T_1 for a field change of 50 kOe are 6, 5.4, 3 and -0.1 J kg^{-1} K^{-1} in the compounds with $x = 0$, 0.4, 0.6 and 1, respectively. A similar decrease in the MCE has been observed in $Gd_{1-x}Sm_xMn_2Si_2$ compounds as well [24]. Figure 4 also shows that the MCE associated with the transition at T_2 remains almost unchanged with Sm substitution. This is because of the fact that the rare earth sublattice magnetic entropy is almost completely released well below T_2 and that the entropy change at T_2 is completely associated with the Mn sublattice. The maximum entropy changes at this transition are found to be -1, -1.1 and -1.3 J kg^{-1} K^{-1} for a field change of 50 kOe, for the compounds with $x = 0.4$, 0.6 and 1 respectively.

In conclusion, we find that the magnetic and magnetocaloric properties of $Gd_{1-x}Sm_xMn_2Ge_2$ correlate very well. The admixture effect of crystal-field levels of the Sm^{3+} ion and the canted magnetic structure of the Mn sublattice may be responsible for the unusual MCE behavior of the Sm-containing compounds. The temperature variation of magnetization in the re-entrant ferromagnetic phase also points towards such a possibility. The magnetocaloric effect is found to decrease with Sm concentration due to the lower magnetic moment of Sm as compared to that of Gd.

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