Frozen magnetostructural order in Gd_5Ge_4: A calorimetric study

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(Received 14 September 2007; revised manuscript received 14 January 2009; published 18 February 2009)

Temperature and magnetic field dependencies of heat capacity C of Gd_5Ge_4 are presented. The arrest of kinetics of the first-order antiferromagnetic to ferromagnetic transition results in a broad peak in magnetic C/T at ≈ 15 K. The corresponding magnetic entropy S_m reduces when magnetic field is applied due to the appearance of ferromagnetism and becomes zero for the fully magnetized state. Anomalous behavior of C in cycling across the antiferromagnetic to ferromagnetic transition is observed. These features are discussed in the framework of different possible mechanisms. Evidence for magnetoelastic coupling is seen from the change in entropy ΔS_H for a change in field across the magnetostructural transition.

DOI: 10.1103/PhysRevB.79.052402 PACS number(s): 75.30.Kz, 65.40.Ba, 75.50.Cc

Gd_5Ge_4 has been studied extensively due to its unusual magnetic properties.[1–8] In the zero magnetic field, Gd_5Ge_4 is antiferromagnetic (*AFM*) below $T_N \approx 125$ K. A transition to ferromagnetic (*FM*) state is observed at $T_c < T_N$ in the presence of a sufficient magnetic field H.[8] This transition is coupled with a martensiticlike structural change.[3,4] The absolute change in entropy across this transition shows a peak in its temperature dependence.[9] Due to this large magnetocaloric effect, such first-order magnetostructural transitions have been attractive for more than a decade for their possible applications in magnetic cooling.[3]

Recently, arrest of kinetics of the AFM to FM transition below a characteristic temperature $T^K \approx 20$ K was demonstrated to be due to the appearance of glassy phase.[1] In this phase, any energy fluctuation, however small it is, induces a stable FM state.[2] Once the FM state is attained, it remains in the same state as long as the temperature is maintained below T^K.[1–8] This irreversibility can be found in different physical properties such as magnetization,[3] x-ray diffraction (*XRD*),[3] differential scanning calorimetry (*DSC*),[10] etc. In this Brief Report, we report on a detailed heat-capacity (C) investigation on Gd_5Ge_4 in the H-T plane. We show here that for temperatures below T^K, there is an abrupt drop in C at a field H^K and it approximately remains at that value even after reducing the field to zero. The entropy associated with the metastable AFM state below T^K is removed by the application of a field above H^K. Our direct measurement of the absolute change in entropy across the T_c shows the evidence for magnetoelastic coupling.

Few reports on heat capacity of Gd_5Ge_4 are found in the literature.[5,8,11,12] No anomaly is observed in the zero magnetic field except at T_N.[8,11,12] For fields above 20 kOe, a peak in temperature dependence of C is observed at T_c.[8] The appearance of glassy phase when temperature is decreased below T^K is seen as a characteristic peak[8] at T^K in magnetic C/T as

$$\Delta C_H/T = (C_{0\ \mathrm{kOe}} - C_H)/T. \quad (1)$$

An irreversible jump in C is observed when $H > 20$ kOe is applied at 2 K.[12] The DSC results show that a certain amount of heat is released when field is increased, indicating that the transition to FM is exothermic.[10] The irreversibility of the transition below T^K is seen as no peak in DSC for the case of field decreasing. However, precise and systematic study on heat capacity of Gd_5Ge_4 is not available in the literature.

The polycrystalline Gd_5Ge_4 and La_5Ge_4 samples were prepared in an argon arc furnace using 99.9% purity Gd and La and 99.999% purity Ge. XRD results show that the samples are in phase pure form. Heat capacity is measured by relaxation technique using Quantum Design 14 T physical properties measurement system (PPMS). The Gd_5Ge_4 is characterized by $M(H)$ at 5 K, resistivity, and thermopower measurements.[13] The results are in par with the literature.[1–8] The $M(H)$ at 5 K shows that 45% of this sample has been converted into FM at fields below 10 kOe. This is a common feature in samples prepared by 99.9% purity of the commercial grade Gd.[10,12,14,15]

Figure 1 shows the $C(T)$ of Gd_5Ge_4 measured at constant H in heating mode after cooling to 2 K in zero field from 200 K. The curves are shifted accordingly for more clarity. The $C(T)$ for $H < 20$ kOe are similar. For fields 30 kOe and above, a peak is observed at T_c. In order to eliminate the lattice contribution, C of La_5Ge_4 is subtracted from that of Gd_5Ge_4 as

$$\Delta C_G/T = (C_{Gd_5Ge_4} - C_{La_5Ge_4})/T. \quad (2)$$

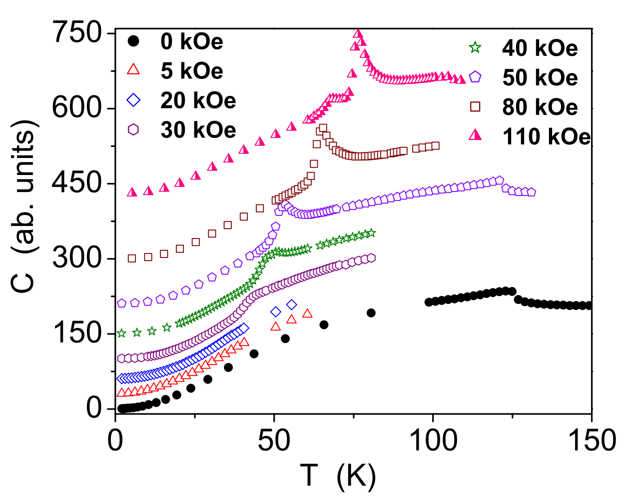

FIG. 1. (Color online) Temperature dependence of heat capacity at various magnetic fields. The values, in J/mol K, of heat capacity corresponding to magnetic fields are shifted vertically for more clarity.

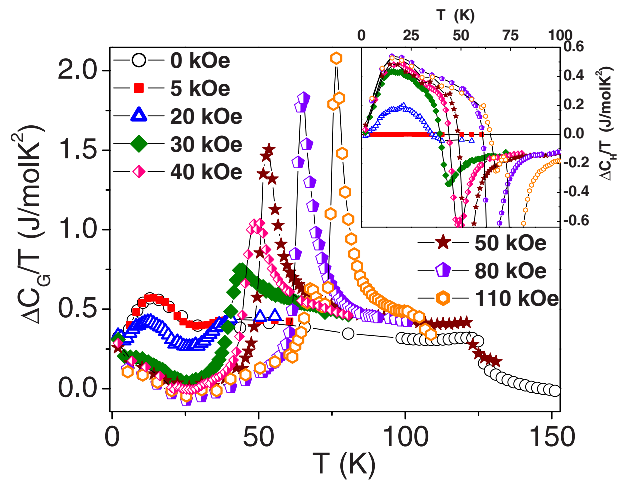

FIG. 2. (Color online) Magnetic heat capacity calculated by subtracting the heat capacity of La_5Ge_4 at 0 kOe from that of Gd_5Ge_4. (Inset) Magnetic field contribution to the heat capacity of Gd_5Ge_4. Heat capacity of Gd_5Ge_4 at 0 kOe is subtracted from that at various fields.

In Fig. 2, we have plotted $\Delta C_G/T$. The inset of Fig. 2 shows the $\Delta C_H/T$ which highlights the effect of magnetic field. A hump around $T^K \approx 15$ K is in par with the earlier reports.[8] This hump is due to the entropy associated with the glassy phase. No phase change at low fields is evident from the indifferent data between zero field and that of 5 kOe. The height of the hump in $\Delta C_G/T$ at 15 K reduces for $H = 20$ kOe. It is interesting to note that at low temperatures $\Delta C_G/T$ approaches zero and $\Delta C_H/T$ follows a single envelop for $H > 30$ kOe. This is because the Gd_5Ge_4 will be at fully saturated magnetization. A small peak appears at 65 K for 110 kOe before the magnetostructural transition at 75 K. This signifies the short-range correlations present in high magnetic fields at high temperatures.[16]

Figure 3 shows the $C(H)$ measured as a function of increasing and decreasing field at 5 and 25 K after cooling in zero field from 200 K. The $C(H)$ at 5 K is constant up to ≈ 15 kOe. It decreases slowly up to 25 kOe and drops suddenly at this field to about 50% of its zero-field value. The value of the $C(H)$ remains more or less same even after removing the field as long as temperature is maintained below 10 K. Such a drop at 25 K reduces to about 10%. Partial recovery of the low field phase is seen as the virgin curve and the second field increasing curves merge above $H = 20$ kOe.

The field-induced metamagnetic transitions and the associated arrest of kinetics have been also studied in other systems such as $CeFe_2$,[17] manganites,[18] Mn_2Sb,[19] Nd_7Rh_3,[20] etc. Phenomenological phase diagrams have been proposed on the basis of experimental results.[18] There are two characteristic fields below T^K, viz., H_1 below which the system will be in metastable state and H_2 above which system enters into stable state. For fields $H_1 < H < H_2$, the metastable state will coexist with the stable state. In the case of Gd_5Ge_4, we can see from $C(T)$ and $C(H)$ data that H_1 is ≈ 15 kOe and H_2 is ≈ 25 kOe.

We can calculate directly from C the entropy S_m associated with the glassy phase and the change in entropy ΔS_H across the magnetostructural transition for a change in field from 0 kOe to a final field H as

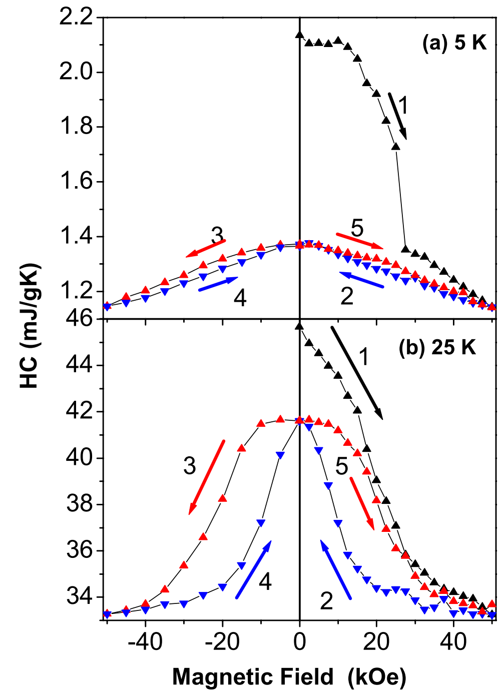

FIG. 3. (Color online) Magnetic field dependence of heat-capacity measurements at constant temperatures of (a) 5 and (b) 25 K. At 5 K, $C(H)$ is constant up to 15 kOe. It gradually decreases between 15 and 25 kOe and then drops suddenly. Then $C(H)$ remains the same even after removing the field as long as the temperature is maintained below 10 K. At 25 K partial recovery is observed.

$$S_m = \int_0^T (\Delta C_G/T)dT \tag{3}$$

and

$$\Delta S_H = S_{0\ \mathrm{kOe}} - S_H = \int_0^T (\Delta C_H/T)dT. \tag{4}$$

Figure 4 shows the S_m as a function of temperature for different H. In the zero field, S_m increases monotonically up to T_N and saturates thereafter. S_m for 5 kOe is the same as that for zero magnetic field. For fields $H > H_2$, S_m is zero for temperatures below T_c. The S_m recovers partially above T_c; however, it recovers fully only above T_N. For 20 kOe ($H_1 < H < H_2$), reduction in S_m at low temperature can be found due to the FM component. Inset of Fig. 4 shows the ΔS_H calculated as a function of temperature. A peak in ΔS_H at T_c signifies the magnetocaloric nature of this transition. This is in par with those reported in the literature.[9]

Figure 5 shows the $C(H)$ at 45, 65, and 121 K. As usual, the sample is first cooled in 0 kOe from 200 K to the final temperature of interest. For the $C(H)$ at 45 and 65 K a huge peak is observed for the FM to AFM transition during field decreasing. However, no peak corresponding to the AFM to

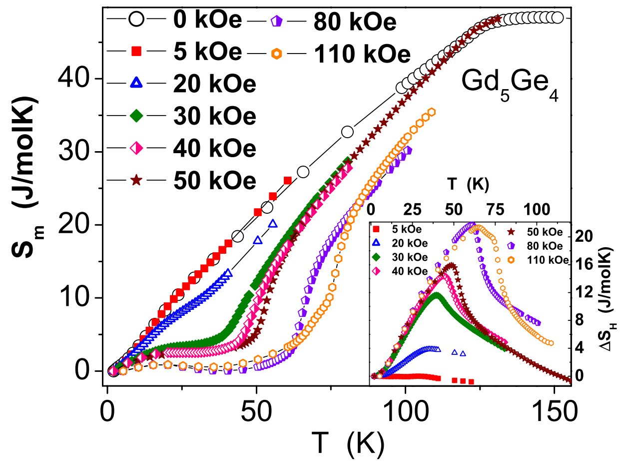

FIG. 4. (Color online) Magnetic entropy S_m is calculated from $\Delta C_G/T$. In the presence of magnetic field, the appearance of FM phase reduces the entropy of the system at low temperatures. (Inset) The entropy change between zero field and an applied field shows a peak indicating magnetocaloric nature of the transition.

FM transition is observed in field increasing cycle. At these temperatures, the transition is completely reversible. The difference between the C values of zero field before and after the application of magnetic fields reduces to less than 2%. At 121 K, there is no difference between virgin field increasing and field decreasing curves below 60 kOe. A transition from AFM to PM is observed at about 50 kOe. Also we observe a small hysteresis above 60 kOe. This hysteresis has the routes to short-range correlations in the presence of high magnetic fields at high temperatures of the order of 100 K.[16] This is supported by the two-peak structure in $C(T)$ at 110 kOe.

We have shown earlier a schematic of the low-temperature phase diagram for Gd_5Ge_4 based on our results[13] and the available phenomenological phase diagrams for arrest of kinetics.[18] According to this model the ground state of Gd_5Ge_4 is FM hindered by the glass transition. The H_1 and H_2 are defined by the lower and upper limits of the crossover between the kinetic arrest band ($H^K T^K$) and the super cooling band ($H^* T^*$). As said earlier, H_1 is ≈ 15 kOe and H_2 is ≈ 25 kOe. Below 15 kOe, temperature dependencies of physical properties for cooled in zero field are similar to measurements at zero field. At these fields when cooled below T_N, T^K appears first than the T^*. This means that the high-temperature AFM phase freezes before it converts into the stable FM state. However, any of the energy fluctuations such as field cycling or temperature cycling at temperatures well below T^K will lead to a state for which $T^K < T^*$.[21] Hence, below 10 K, zero-field state after field cycling above 25 kOe is the same as cooling the specimen in fields above 25 kOe. Cooling the specimen below 10 K with a field between 15 and 25 kOe leads to the coexistence of metastable AFM state along with the stable FM state. The effect of H_1 and H_2 can be seen clearly on the heat capacity. The $C(H)$ at 5 K is constant up to 15 kOe while $\Delta C_G/T$ remains same for 0 and 5 kOe along with zero $\Delta C_H/T$. For fields above 25 kOe, $C(H)$ at 5 K is almost constant with 50% of its zero-field value and $\Delta C_G/T$ becomes zero (zero magnetic entropy) along with a single envelop in $\Delta C_H/T$ below T_c.

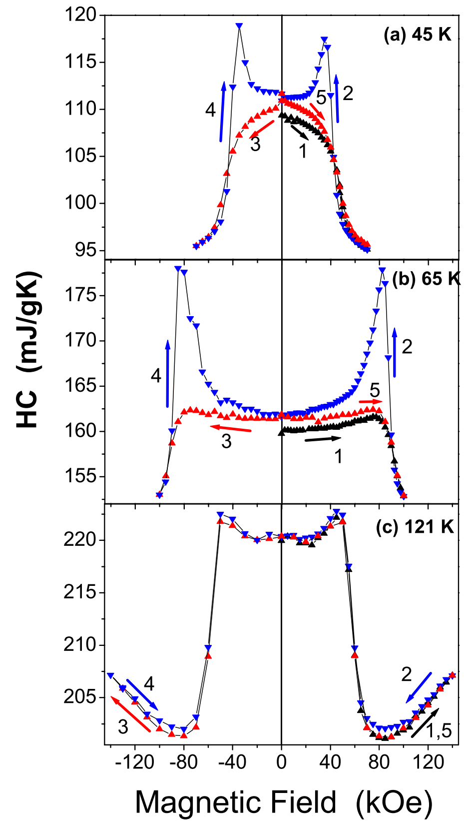

FIG. 5. (Color online) Magnetic field dependence of heat-capacity measurements at constant temperatures of (a) 45, (b) 65, and (c) 121 K. Transition from AFM to FM shows no peak structure, while a huge peak is observed during reverse cycle for 45 and 65 K. At 121 K, AFM to paramagnetic (PM) transition is observed at 50 kOe.

It is interesting to note that at 45 and 65 K, anomalous difference in field dependencies of heat capacity for field increasing and field decreasing are observed even though the transition from FM↔AFM is completely reversible in this

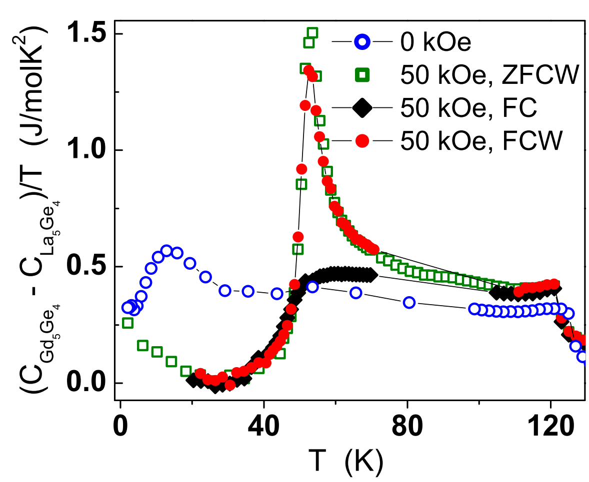

FIG. 6. (Color online) Heat capacity measured during ZFC, ZFCW, FCC, and FCW at 50 kOe. Here also transition from AFM to FM shows no peak structure, while a huge peak is observed during reverse cycle.

regime. In order to understand this, we have carried out temperature runs in zero-field cooling (ZFC), zero-field-cooled warming (ZFCW) at 50 kOe, field cooling (FCC) at 50 kOe, and field-cooled warming (FCW) at 50 kOe (Fig. 6). Interestingly we get similar results. During FCC no peak appears for the AFM to FM transition while in ZFCW and FCW we find a peak corresponding to the FM to AFM transition. Hence, possibility of intrinsic error due to relaxation technique[22,23] may be ruled out. Other possibilities are (i) since some FM components are present at 0 kOe, AFM to FM transition happens by homogeneous nucleation while reverse is by heterogeneous nucleation and (ii) the ground state of the Gd_5Ge_4 is FM. Hence the energetics involved in the AFM to FM and FM to AFM transitions is different.[10] However it is not possible within this frame of work to distinguish between the two.

The change in entropy across T_c, calculated from magnetization, is purely magnetic in origin, while ΔS_H calculated from heat capacity involves all the contributions, in this case, the entropy associated with the structural transition as well as FM$\leftrightarrow$AFM transition. For Gd_5Ge_4, the values of ΔS_H calculated from heat-capacity measurements agree well with that calculated from the magnetization measurements.[16] This is one of finest examples of magnetoelastic coupling. Double peak structure in ΔS_H at 110 kOe is similar to that reported in the literature,[16] indicative of the existence of short-ranged FM and AFM correlations.

Authors acknowledge P. Chaddah for introducing the concept of kinetic arrest to us and for his encouragement and helpful discussion, and A. Banerjee for magnetization measurements. DST, India is acknowledged for funding 14T/0.3K PPMS and 14T VSM. L.S.S.C. and D.J. would like to thank CSIR, India and S.P. and P.N.V. would like to thank DST, India for financial support. Staff of the LTL and cryogenics is acknowledged. Ajay Gupta, R. Srinivasan, B. A. Dasannacharya, and V. N. Bhoraskar are acknowledged for their encouragement.

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