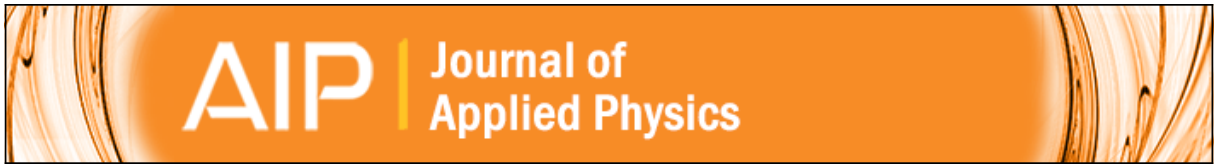

Isothermal variation of the entropy (Δ S T) for the compound Gd 5 Ge 4 under hydrostatic pressure

A. Magnus G. Carvalho, A. A. Coelho, S. Gama, P. J. von Ranke, and C. S. Alves

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Isothermal variation of the entropy (ΔS_T) for the compound Gd_5Ge_4 under hydrostatic pressure

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In the present work, the isothermal variation of the entropy (ΔS_T) for the compound Gd_5Ge_4 was studied at different applied hydrostatic pressures (from 0 up to 0.58 GPa). In all pressure ranges, we observe the giant magnetocaloric effect. The ΔS_T data for the compound Gd_5Ge_4 at zero applied pressure present two peaks: the lowest temperature peak is due to irreversible processes and the highest temperature peak is due to magnetostructural transitions. Increasing the pressure, the lowest temperature peak displaces to lower temperatures and disappears. The magnitude of the other peak has a nonlinear behavior with pressure. Different protocols were used to obtain ΔS_T at zero applied pressure and the results indicate that ΔS_T strongly depends on the initial and final states of Gd_5Ge_4 compound. We also present a *T-P* magnetic phase diagram built from the available magnetic data.
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I. INTRODUCTION

The isothermal variation of the entropy (ΔS_T) is one of the parameters that characterize the magnetocaloric effect (MCE) in the magnetic materials. MCE is an essential physical phenomenon for the magnetic refrigeration.[1,2] Since the discovery of the giant MCE (GMCE) in the compound $Gd_5Ge_2Si_2$ around room temperature,[3] the series $Gd_5(Ge_{1-x}Si_x)_4$ has become the most studied family of magnetocaloric materials.

The compound Gd_5Ge_4 was the first one of the family $Gd_5(Ge_{1-x}Si_x)_4$ studied under different hydrostatic pressures by Magen *et al.*[4] in 2003. Besides the interesting linear thermal expansion results, these scientists also studied the magnetization in different pressures as a function of the temperature and magnetic field. In contrast with the magnetic behavior of the Ge rich compounds with $0<x\leq 0.3$, no ferromagnetic phase is observed in Gd_5Ge_4 at zero magnetic field and down to the lowest measured temperature.[5,6] This compound orders antiferromagnetically below ~130 K and has the type II orthorhombic structure [O(II)]. Induced by the magnetic field, there is a magnetostructural transition from the antiferromagnetic O(II) phase to the ferromagnetic phase, which has the type I orthorhombic structure [O(I)].[7–10] In the structure O(I) all subnanometers layers (slabs) are interconnected via partially covalent bonds among Ge and Si atoms, while none remain in the structure O(II). Magen *et al.*[4] showed that the effect of the hydrostatic pressure is similar to the one produced by the magnetic field, e.g., the pressure also induced the transition from the antiferromagnetic O(II) phase to the ferromagnetic O(I) phase.

In 1997, Pecharsky and Gschneidner[11] reported their results on the isothermal variation of the entropy as a function of the temperature for Gd_5Ge_4 with zero applied pressure. The MCE curve presents two peaks, which were not discussed. In spite of the interesting results for this compound under hydrostatic pressures, there are no MCE studies for $P\neq 0$. The aim of the present work is to study the influence of the hydrostatic pressure on the magnetocaloric properties of the compound Gd_5Ge_4.

II. EXPERIMENTAL PROCEDURES

The compound Gd_5Ge_4 was prepared using Gd, 99.99 wt % pure (metals and interstitial), and semiconductor grade Ge, 99.9999 wt % pure (metals and interstitial), by arc melting for three times to guarantee the sample homogeneity. The mass of the sample was 5 g and there was no relevant weight loss. The sample was qualitatively analyzed by metallography and a tiny amount of a second phase, probably Gd_5Ge_3, was observed.

The magnetization measurements under pressure were performed in a superconducting quantum interference device magnetometer (Quantum Design) in magnetic fields up to 70 kOe in the temperature range from 4 to 170 K. We have used a nonmagnetic Cu–Be clamp-type cell, able to work up to 1.2 GPa at 300 K. The sample was inserted in a Teflon® container filled with mineral oil. A piece of lead was used as a manometer and the pressures reported in this work were obtained at low temperatures.

The isothermal variation of the entropy (ΔS_T) shown in Fig. 2 for the different pressures was calculated from the isothermal magnetization data. We have performed a usual protocol (now on called *Protocol 1*).

Protocol 1. Before each isotherm, the magnetic field is removed, the temperature is stabilized, and an isothermal

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magnetization curve is measured increasing the magnetic field until 50 kOe. The subsequent temperatures of the isotherms are always higher than the previous temperature. To obtain ΔS_T data presented in Fig. 7, we have used other three different protocols for Gd_5Ge_4 compound at zero applied pressure.

Protocol 2. Before each isothermal magnetization curve, the magnetic field was removed, the sample was heated up to 80 K, and after that cooled down to the temperature in which we would perform the measurement from 0 up to 50 kOe (similar to the protocol proposed in Ref. 12). The subsequent temperatures of the isotherms are always higher than the previous temperature.

Protocol 3. Before each isofield magnetization curve, the magnetic field was removed, the sample was heated up to 80 K, and after that cooled down to 4 K. Isofields were measured by increasing the temperature at fixed magnetic fields from 0 up to 50 kOe.

Protocol 4. Before each isofield magnetization curve, 50 kOe magnetic field was applied at 4 K (initial temperature of measurement) and after that the magnetic field was reduced to the magnetic field of interest. Isofields were measured by increasing the temperature at fixed magnetic fields from 0 up to 50 kOe.

To calculate ΔS_T from isothermal magnetization data, we have used the following relation:

$$\Delta S_T(T)_{\Delta H} = \frac{1}{2\delta T}\left(\delta M_1 \delta H_1 + 2\sum_{k=2}^{n-1} \delta M_k \delta H_k + \delta M_n \delta H_n\right), \tag{1}$$

which was discussed elsewhere.[13,14] To calculate ΔS_T isofield magnetization data, we have used the following relation:

$$\Delta S_T(T_k)_{\Delta H} = \sum_{i,j} \frac{1}{2}\left[\left(\frac{\partial M_i}{\partial T_k}\right)_{H_i} + \left(\frac{\partial M_j}{\partial T_k}\right)_{H_j}\right]\Delta H_{ij}, \quad j = i + 1. \tag{2}$$

In the relation (2), M_i and M_j are the experimental values of the magnetization at applied magnetic fields H_i and H_j, respectively, and temperature T_k; $\Delta H_{ij}=H_j-H_i$ is the magnetic field step, which can be variable from 0 up to 50 kOe.

III. RESULTS AND DISCUSSION

In Fig. 1, we show the magnetization as a function of the temperature for the compound Gd_5Ge_4 at different hydrostatic pressures. With zero applied pressure, the feature of the magnetization is similar to those reported previously in the literature.[4,7] At 0.03 GPa, no significant change was observed in the magnetization curves, so it was omitted in the Fig. 1. Increasing the pressure, we note that a first-order magnetostructural transition appears, and the transition is displaced to higher temperatures, as it was reported elsewhere.[4] Our data show that the displacement of the transition temperature is $dT_t/dP \cong 45$ K/GPa, in good agreement with Magen *et al.*,[4] who determined $dT_t/dP \cong 49$ K/GPa from their magnetization data. The inset of Fig. 1 shows in detail the $M \times T$ curves around the Néel temperature at different pressures. Considering the experimental errors, we do not observe any

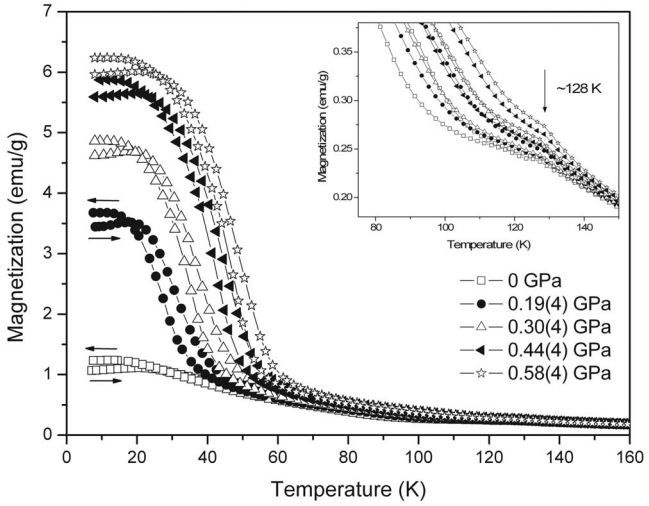

FIG. 1. Magnetization as a function of the temperature for the compound Gd_5Ge_4 at external magnetic field of 200 Oe and different applied hydrostatic pressures. The magnetization was measured heating up and cooling down. The inset shows details around Néel temperature.

displacement of the Néel temperature (~128 K) with the increasing hydrostatic pressure. It is not in agreement with Magen *et al.*,[4] who obtained the rate $dT_N/dP \cong 7$ K/GPa.

In Fig. 2, we present the results of MCE, isothermal variation of the entropy (ΔS_T), for the compound Gd_5Ge_4 at different hydrostatic pressures and magnetic field variation from 0 to 50 kOe. It is worth noticing the existence of two peaks in MCE data, even for the sample with zero applied pressure. Data for zero applied pressure are in good agreement with that reported by Pecharsky and Gschneidner.[11] The highest temperature peak (43 K) is related to the magnetostructural transitions observed in $M \times T$ curves, such as that reported in Fig. 2 of Ref. 5. The lowest temperature peak (11 K) is originated from a partial reversibility that Gd_5Ge_4 compound presents and can be better understood when we analyze the isotherms of Fig. 3.

The magnetization isotherms of Fig. 3 were measured from 4 to 26 K at intervals of 2 K and from 30 to 78 K at

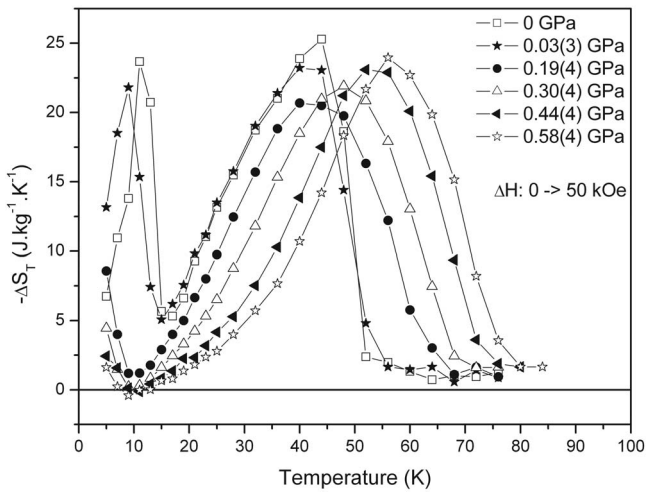

FIG. 2. Isothermal variation in the entropy as a function of the temperature at different hydrostatic pressures. The curves were calculated from the magnetization isotherms from 0 up to 50 kOe.

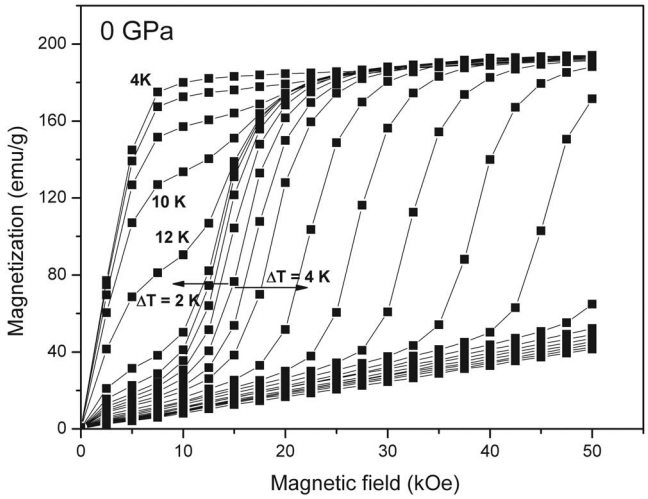

FIG. 3. Magnetization isotherms measured with no applied pressure for the compound Gd_5Ge_4. From 4 to 26 K the isotherms were measured at intervals of 2 K and from 30 to 78 K at intervals of 4 K.

intervals of 4 K. The first two curves have typical ferromagnetic behavior. The next isotherms have the coexistence of ferromagnetic and antiferromagnetic phases even before the metamagnetic transitions, and the amount of the ferromagnetic phase decreases with the temperature, according to Ref. 5. At 10 K, we notice that the reversibility is partial, since the profile of the next isotherm (12 K) indicates that more ferromagnetic phase became antiferromagnetic in the demagnetizing process. These processes more and more reversible with increasing temperature provoke the large variation in the areas among the isotherms and consequently the MCE peak around 11 K, whose magnitude characterizes a GMCE.

With the application of hydrostatic pressure, the peak at 11 K displaces to lower temperatures and disappears. It is worth noticing that, as the lowest temperature peak disappears with the increasing applied pressure, positive values of ΔS_T appear (Fig. 2). For 0.58 GPa, there are three measured/calculated positive values and the largest one is out of any experimental errors. The origin of this inverted MCE is the crossing isotherms shown in the Fig. 4(b). However, these crossings are not induced by pressure, since they are also present in the 0 GPa data, but with zero applied pressure they are not enough to produce positive values of ΔS_T.

The magnitude of the GMCE (ΔS_T) of the second peak decreases with pressure until 0.19 GPa. With subsequent increasing pressure until 0.58 GPa, the GMCE turns to increase almost reaching the value at zero applied pressure. This behavior is different from that observed for $Gd_5Ge_2Si_2$ compound[15] whose GMCE continuously decreases with hydrostatic pressure and stops being a giant effect. The peak temperature almost does not change until 0.19 GPa and displaces to higher temperatures above this pressure.

For applied pressure of 0.58 GPa, the sharp metamagnetic transitions disappear [Fig. 4(a)]. It could be an indication of disappearance of the first-order character of the transitions at this hydrostatic pressure, but the hysteresis in the $M \times T$ data (Fig. 1) and the high peak value of ΔS_T (Fig. 2) indicate the opposite.

Another important parameter to analyze magnetocaloric

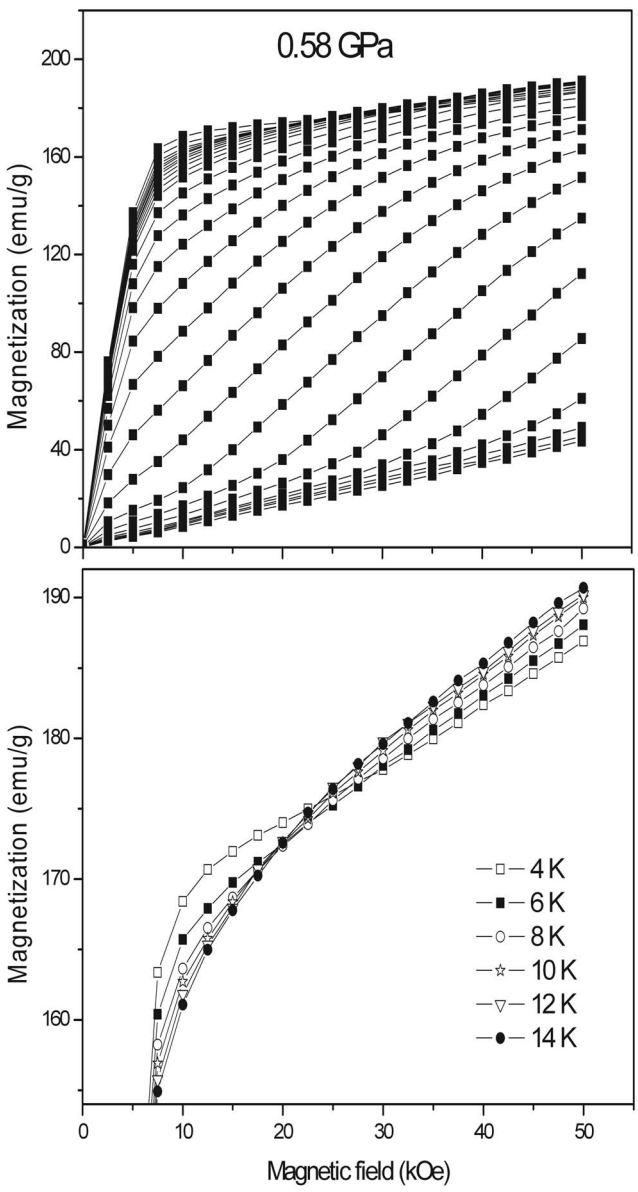

FIG. 4. (a) Magnetization isotherms measured with applied pressure of 0.58 GPa for the compound Gd_5Ge_4. From 4 to 26 K the isotherms were measured at intervals of 2 K and from 30 to 78 K at intervals of 4 K. (b) Detailed isotherms from 4 to 14 K.

materials comparatively is the *refrigeration capacity* (q), which is given by[16,17]

$$q(\Delta T)_{\Delta H} = -\int_{T_1}^{T_2} \Delta S_T(T)_{\Delta H} dT, \tag{3}$$

where ΔH is the variation in the magnetic field used to calculate ΔS_T, T_1 is the temperature of the cold end of a refrigeration cycle, T_2 is the temperature of the hot end, and $\Delta T = T_2 - T_1$. In fact, q is the area under $\Delta S_T \times T$ curve and quantifies the maximum heat that can be transferred from the cold end (T_1) to the hot end (T_2). To compare different materials, we must often calculate q for a similar and convenient ΔT.[17,18] Neglecting the errors in ΔS_T, we plot the refrigeration capacity as a function of the pressure in Fig. 5. q was calculated with $\Delta T = 51$ K around the highest temperature peak of each ΔS_T curve. Considering a linear fit, we find that

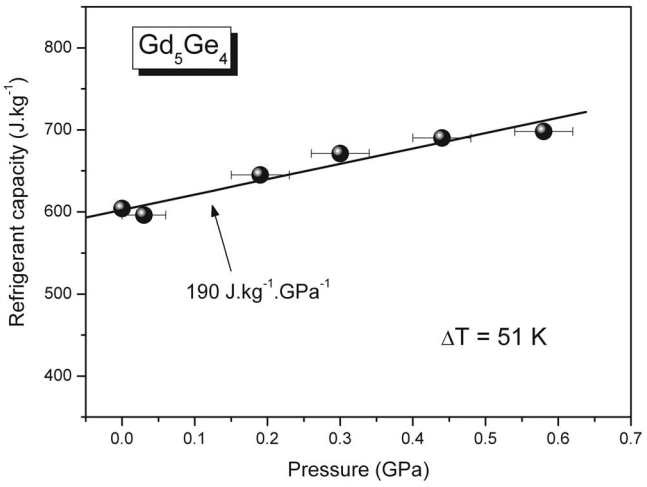

FIG. 5. Refrigeration capacity as a function of the hydrostatic pressure calculated with 51 K around the peak temperature of the $\Delta S_T \times T$ curves.

the refrigeration capacity increases with pressure at a rate of $q/P = 190$ J kg^{-1} GPa^{-1}, varying from 600 J kg^{-1} at 0 GPa up to 700 J kg^{-1} at 0.58 GPa.

With the available data, we are able to outline a *T-P* magnetic phase diagram for Gd_5Ge_4, which is represented in Fig. 6. This diagram was built from the heating curves of $M \times T$ data. We can clearly distinguish four regions. One of them is the paramagnetic phase above 128 K. Below 128 K, there is an antiferromagnetic phase, whose lower limit in temperature is a region of phase coexistence. Since the $M \times T$ curve at 0.03 GPa is almost identical to the one at 0 GPa, e.g., 0.03 GPa is not enough to induce ferromagnetic coupling, we can affirm that the antiferromagnetic phase exists at low temperatures and low hydrostatic pressures. At low temperatures, the upper limit in pressure for the antiferromagnetic phase is not well established, but it is at most 0.13 GPa, since Magen *et al.*[4] reported induction of ferromagnetic

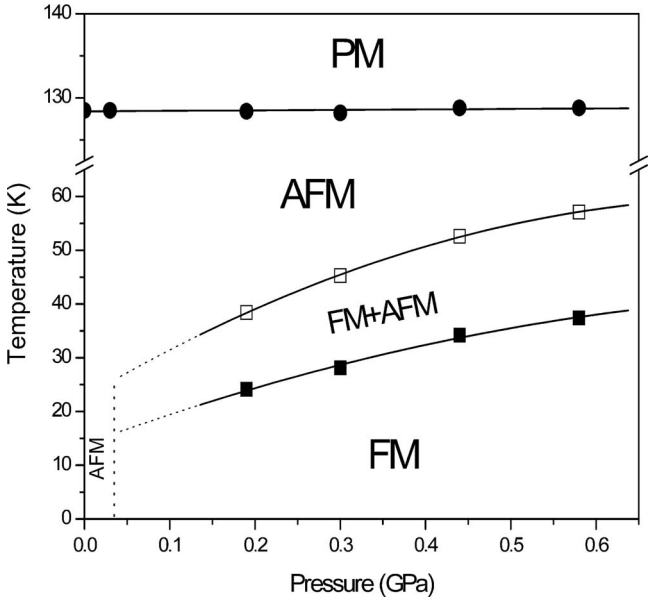

FIG. 6. *T-P* magnetic phase diagram for the compound Gd_5Ge_4 built from $M \times T$ data (heating data). The solid lines are guides to the eyes and the dotted lines are supposed extensions of the experimental data.

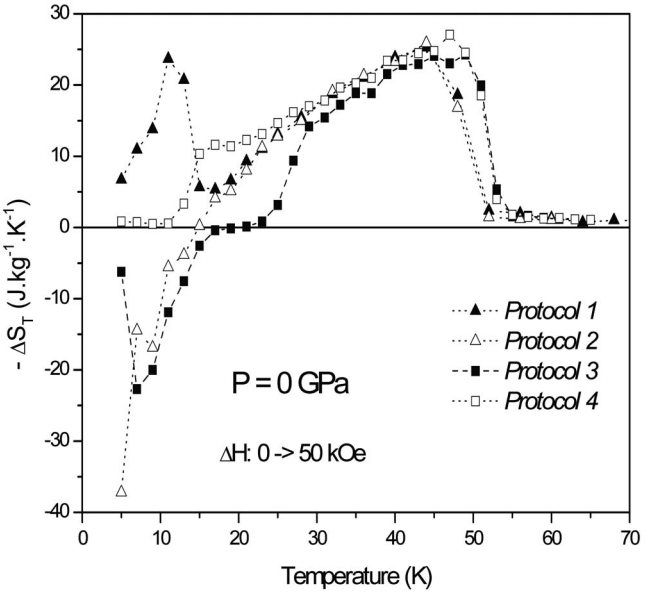

FIG. 7. Isothermal variation in the entropy for Gd_5Ge_4 compound at zero applied pressure obtained from four different protocols described in the Experimental procedures section. Protocols 1 and 2 used isothermal curves ($M \times H$) and protocols 3 and 4 used isofield curves ($M \times H$).

phase at this pressure. From our data, at low temperatures and above 0.03 GPa, there is a ferromagnetic phase. According to the Ref. 4, this phase exists at low temperatures until 0.8 GPa at least. Increasing the temperature from the ferromagnetic phase, we achieve a region of coexistence between the ferromagnetic and antiferromagnetic phases, which was determined from the heating $M \times T$ data.

Since the ΔS_T peak at low temperature shown in Fig. 2 is due to irreversible processes at zero and low applied pressures, we performed other magnetization measurements ($M \times H$ and $M \times T$) at zero applied pressure with different procedures to verify the possible different ΔS_T profiles. In Fig. 7, we present ΔS_T results obtained from protocols 1–4 described in the Experimental procedures section. For the range of temperatures where there is partial or total irreversibility, below ~20 K, it is easy to see that there are great divergences among ΔS_T profiles for the four analyzed protocols. We also notice differences next to the highest temperature maxima around 45 K. ΔS_T magnitudes for protocols 1 and 2 decrease faster than that for protocols 3 and 4. This can be partially explained by the relatively large ΔT interval between the two consecutive isotherms, which have transitions around 50 kOe, used in the protocols 1 and 2, as shown in Fig. 3 (Protocol 1). Other contribution to these differences would be irreversible processes around the first-order transitions. Such differences are also observed in the MnAs compound[19] and probably in other magnetocaloric materials that present first-order transitions.

Based on $M \times T$ data reported by Tang *et al.*,[7] we expect that Gd_5Ge_4 presents a positive ΔS_T at low temperatures. This way, the protocols 2 and 3 could be candidates to the protocol that best reflects the intrinsic properties of this compound. Nevertheless, magnetic refrigeration can use several thermodynamical cycles. If the initial and final states of processes are different in certain thermodynamical cycles, ΔS_T

could have very different values. So, it is not obvious to indicate which is the correct protocol for calculating the isothermal variation in the entropy in the case of Gd_5Ge_4 and probably other compounds that present first-order transitions.

IV. CONCLUSIONS

The MCE of the compound Gd_5Ge_4 at zero applied pressure presents two peaks: the lowest temperature peak is due to irreversible processes and the highest temperature peak is due to magnetostructural transitions. Increasing the pressure, the lowest temperature peak displaces to lower temperatures and disappears, which is an indication that irreversibility disappears with applied pressure. The magnitude of the other peak decreases with pressure until 0.19 GPa. With subsequent increasing pressure until 0.58 GPa, the magnitude turns to increase almost reaching the value at zero applied pressure. In all pressure range, we observe GMCE, and the refrigeration capacity increases with the applied pressure.

From the available magnetic data, we built a *T-P* magnetic phase diagram for Gd_5Ge_4. Besides the magnetic single phase regions (paramagnetic, ferromagnetic, and antiferromagnetic), there is also a region in the diagram where ferromagnetic and antiferromagnetic phases coexist. The temperature range of coexistence increases with hydrostatic pressure.

ΔS_T obtained from the different protocols at zero applied pressure present great divergences. These divergences are consistent with the fact that ΔS depends on the initial and final states of the system.

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