# Magnetocaloric and barocaloric effects in a $Gd_5Si_2Ge_2$ compound*

Zou Jun-Ding(邹君鼎)†

*School of Materials Science and Engineering, Beihang University, Beijing* 100191, *China*

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The first-order phase transition in $Gd_5Si_2Ge_2$ is sensitive to both magnetic field and pressure. It may indicate that the influences of the magnetic field and the pressure on the phase transition are virtually equivalent. Moreover, theoretical analyses reveal that the total entropy change is almost definite at a certain Curie temperature no matter whether the applied external field is a magnetic field or a pressure. The entropy change curve can be broadened dramatically under pressure, and the refrigerant capacity is improved from 284.7 J/kg to 447.0 J/kg.

**Keywords:** magnetic phase transformation, magnetic properties, magnetocaloric effect

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## 1. Introduction

The discovery of giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$[1,2] extensively promotes the research on magnetocaloric materials and the magnetic refrigeration technique. Since then, many magnetocaloric materials[3−15] and magnetic refrigeration prototype instruments[16−18] have been reported. The MCE originates from the change in the microscopic magnetic order induced by an applied magnetic field, and is marked by the isothermal entropy change or the adiabatic temperature change. The performance of a magnetic refrigerant relies on the size of the MCE and the strength of the magnetic field. It should be noted that the rather high magnetic field usually required for magnetic refrigeration may impede the practical application to be realized simply and reliably. As for materials with large MCE, they have one common peculiarity that their first-order phase transitions are sensitive to several external parameters, such as magnetic field, temperature, and pressure. This feature may be of great benefit to improve the performance of magnetocaloric materials and develop new magnetic refrigeration instruments. The following discussion will reveal the potential advantages of magnetocaloric materials theoretically and experimentally, and develop a method to evaluate the caloric effect during a first-order phase transition under both a magnetic field and hydrostatic pressure.

Note that all giant MCEs are observed in the vicinity of first-order phase transitions and the phase transition temperatures are very sensitive to the magnetic field or the pressure. Indeed, these phenomena reflect the internal intrinsic coupling effect between the magnetic and the structural degrees of freedom, termed the magnetostructural (or magnetoelastic) coupling effect. This unique feature provides a scarce possibility to manipulate the phase transition flexibly. As a result, not only the applicabilities of magnetocaloric materials may be enhanced, but also the MCE and the magnetic refrigerant capacity (RC) may be improved. Oliveira *et al.* have theoretically studied the MCE and the barocaloric effect (BCE) of $ErCo_2$[19] and $La(Fe_{0.89}Si_{0.11})_{13}$[20] under pressure and magnetic field, and revealed that the large caloric effect may be obtained in a wide range of temperature. The mechanism of the BCE is similar to that of the MCE described above, while the pressure replaces the magnetic field. Mañosa *et al.* reported the large BCE and MCE in the Ni–Mn–In alloy,[21] which may originate from the discontinuities of volume and entropy. These results indicate that the magnetocaloric materials may have great potential, which has not been fully appreciated. $Gd_5Si_2Ge_2$ is employed to investigate the behavior of the caloric effect under a magnetic field and hydrostatic pressure due to its typical first-order phase transition and giant MCE.

The $Gd_5Si_{4-x}Ge_x$ compounds can form

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†Corresponding author. E-mail: zoujd@buaa.edu.cn

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$Gd_5Si_4$-type, $Gd_5Si_2Ge_2$-type, and $Sm_5Ge_4$-type structures.[7,22,23] The phase transition of the $Gd_5Si_{4-x}Ge_x$ compounds can be controlled by magnetic field, temperature, as well as pressure.[1,2,24–27] Experimental studies show that the giant MCEs observed in the $Gd_5Si_{4-x}Ge_x$ compounds are associated with a field-induced first-order structural transition from the paramagnetic (PM) monoclinic structure to the ferromagnetic (FM) orthorhombic structure.[26] Here we engage in thorough experimental studies of crystallographic, magnetic, and caloric properties of the $Gd_5Si_2Ge_2$ compound, allowing the exploration of the mechanism of the caloric effect. Moreover, a general analysis will be carried out, and a possible theoretical model is developed and used to describe the behaviors of the entropy change under both magnetic field and pressure.

## 2. Experimental details

The $Gd_5Si_2Ge_2$ samples were prepared by arc melting the pure metals under argon atmosphere in a water-cooled copper hearth. The purities of the raw materials were 99.9 wt.% for gadolinium and 99.99 wt.% for silicon and germanium. The samples were sealed in quartz tubes at high vacuum. The samples were annealed at 1393 K for 14 days, and then quenched in liquid nitrogen. The temperature dependence of the polycrystalline X-ray diffraction (XRD) data were collected by using a Bruker D8 diffractometer. The direct-current (dc) magnetization and the heat capacity measurements were performed using a physical property measurement system (PPMS-9T Quantum Design). The magnetic properties under hydrostatic pressure were measured by using a magnetic property measurement system (MPMS, Quantum Design) with an MPMS high pressure capsule cell (Honest Machinery Designer's Office, Japan). The pressure value was determined by the press dependent critical temperature of the superconducting state of the Pb sensor placed inside the cell.

## 3. Results and discussion

The heat-treated $Gd_5Si_2Ge_2$ sample has a monoclinic structure at room temperature.[28] The temperature dependence of XRD confirms the structural transformation from monoclinic to orthorhombic on cooling.[28] The Curie temperature of this sample is 268 K at 50 mT,[28] which is very close to the previous result.[24,29] Here the Curie temperature is defined as the maximum slope of the temperature dependence of magnetization as a function of magnetic field and pressure on heating. As the magnetic field increases, the phase transition point linearly moves to the higher temperature with a slope of approximately 5.7 K/T. The phase transition point is 272 K at 1 T, and reaches 295 K at 5 T.[28] The hydrostatic pressure also can linearly drive the phase transition point to the higher temperature with a slope of approximately 4.8 K/kbar.[24]

The magnetostructural phase transition is a sign of the coupling effect existing between the magnetic and the structural degrees of freedom. In this case, the external parameters, such as the magnetic field and the pressure, may actually play a role of trigger, which can determine the phase transition occurring or not. Therefore, the influences of the magnetic field and the pressure on the phase transition are virtually equivalent. Since the giant MCEs induced by the magnetic field have been observed in the $Gd_5Si_{4-x}Ge_x$ compounds, the giant BCE induced by the pressure is naturally expected. However, the BCE cannot be obtained with ease due to the difficulty in manipulating pressure and detecting the volume change during a measurement. Here we try to describe a simple method, by which the caloric effect can be evaluated under magnetic field and pressure.

For the FM–PM phase transition, there are two cases, as schematically demonstrated in Fig. 1. In the first one, the phase transition point is driven up to a higher temperature by the magnetic field, but is depressed to a lower temperature by the pressure, e.g., $LaFe_{13-x}Si_x$,[30–34] and MnAs.[3,6] In the second one, the phase transition point is promoted to a higher temperature by both the magnetic field and the pressure, e.g., $Gd_5Si_{4-x}Ge_x$[24–27] and $La_{0.69}Ca_{0.31}MnO_3$.[35] Figure 1(a) shows the possible spontaneous magnetization and Curie temperature $T_C$ varying with temperature under magnetic field and hydrostatic pressure. The influence of the magnetic field on $T_C$ is opposite to that of the pressure. It is well known that both the entropy and the spontaneous magnetization can scale the order of the magnetic system. The corresponding entropy changes under the magnetic field will, without doubt, counteract with those under the pressure, as shown in Fig. 1(b). While the entropy changes under the magnetic field will superpose with those under the pressure in the second case.

Figures 1(c) and 1(d) schematically show the possible spontaneous magnetization and entropy changes varying with temperature. The higher the Curie temperature shifts, the wider the entropy change curve is. Certainly, the actual shape of the entropy change curve will depend on the actual magnetic field and pressure. Based on this feature, if the pressure is applied together with the magnetic field, the required magnetic field may be reduced dramatically, while the magnetic RC is retained, and vice versa. This method will enhance the applicabilities and the maneuverabilities of the magnetocaloric materials, especially for $Gd_5Si_{4-x}Ge_x$ compounds. Usually, the entropy change curves shown in Figs. 1(b) and 1(d) cannot be obtained directly, because the pressure and the volume changes cannot be obtained easily. Therefore, it is necessary to develop a simple yet effective theoretical model and an experimental method that can be used to describe the behavior of the caloric effect during a first-order phase transition under both magnetic field and pressure.

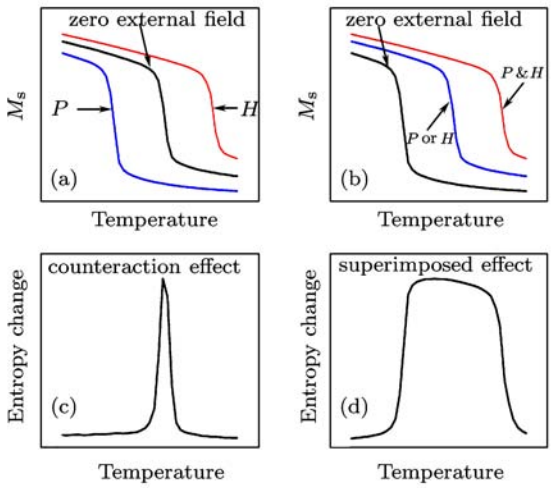



**Fig. 1.** (colour online) Schematic diagrams of temperature dependences of spontaneous magnetization and entropy change. (a) The phase transition temperature is promoted to a higher temperature by the magnetic field, while is depressed to a lower temperature by the hydrostatic pressure. (b) The corresponding entropy change during the phase transition under magnetic field and hydrostatic pressure shown in (a). (c) The phase transition temperature is promoted to a higher temperature by both the magnetic field and the hydrostatic pressure. (d) The corresponding entropy change during the phase transition under magnetic field and hydrostatic pressure shown in (c).

We have previously discussed the mechanism of the entropy change under a magnetic field.[10−13] Here we will expand the discussion by including the behaviors of the entropy change impacted by both magnetic field and hydrostatic pressure. According to the Maxwell relations,[10−13] if the magnetic system is independent, the magnetic entropy change under an applied magnetic field can be expressed as

$$\begin{aligned}\Delta S &= S(H_1, T) - S(H_0, T) \\ &= \int_{H_0}^{H_1} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H, \end{aligned} \tag{1}$$

where $S$ is the entropy, $H$ is the magnetic field, $T$ is the temperature, and $M$ is the magnetization. Equation (1) is widely used to calculate the entropy change under a magnetic field, and the integration can be carried out numerically. Similarly, if the structural system is independent, the baric entropy change under applied pressure can be expressed as

$$\begin{aligned}\Delta S &= S(P_1, T) - S(P_0, T) \\ &= \int_{P_0}^{P_1} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P, \end{aligned} \tag{2}$$

where $P$ is the applied pressure.

In fact, the calculation of Eq. (2) is difficult, which has been mentioned above. It is well known that first-order magnetic phase transitions are often companied by volume deformations and even structural transformations. It indicates that there are strong coupling effects (such as magnetostructural or magnetoelastic coupling), herein both the magnetic and the structural systems are not independent. Therefore the result calculated from Eq. (1) or (2) is virtually the total entropy change of the system, not solely the magnetic entropy change or the baric entropy change. In this case, the amount of the total entropy change is almost definite at a certain Curie temperature no matter whether the external field is a magnetic field or a pressure, i.e.,

$$\Delta S\,(T_{\mathrm{C}}, H) \cong \Delta S\,(T_{\mathrm{C}}, P)\,. \tag{3}$$

This relation is a criterion, and the following experimental method should meet this criterion.

The magnetization isotherms of $Gd_5Si_2Ge_2$ between 256 K and 300 K are shown in Fig. 2(a). The magnetization isotherms at 4.22 kbar are shown in Fig. 2(b). The entropy change $\Delta S$ as a function of temperature and magnetic field is calculated from the magnetization isotherms, and shown in Fig. 3(a). Large spike-like peaks are observed. The mechanism of the spike-like peaks appearing in the vicinity of the first-order phase transition has been previously revealed.[12,13] The peak value of $\Delta S$ reaches 40.2 J/kg · K at 0–5 T. Compared with the sharp peak, the smooth plateau of $\Delta S$ is almost half the height

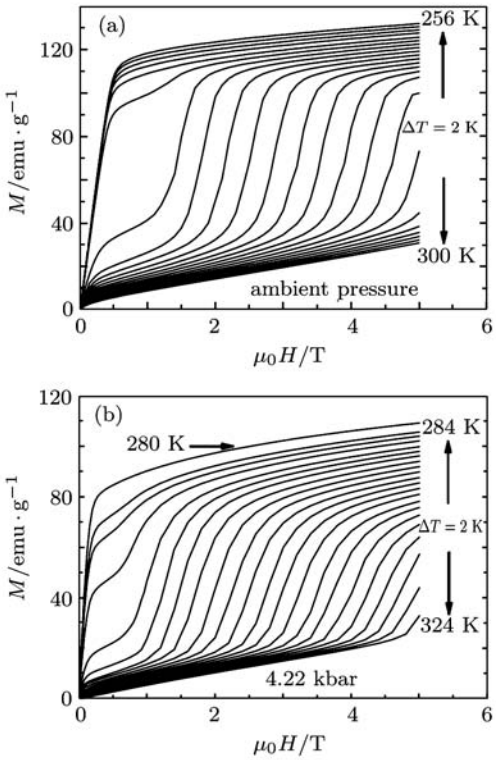



**Fig. 2.** Isothermal magnetizations of $Gd_5Si_2Ge_2$ compound versus applied magnetic field at (a) ambient pressure and (b) 4.22 kbar, where the magnetizations are measured under an increasing magnetic field.

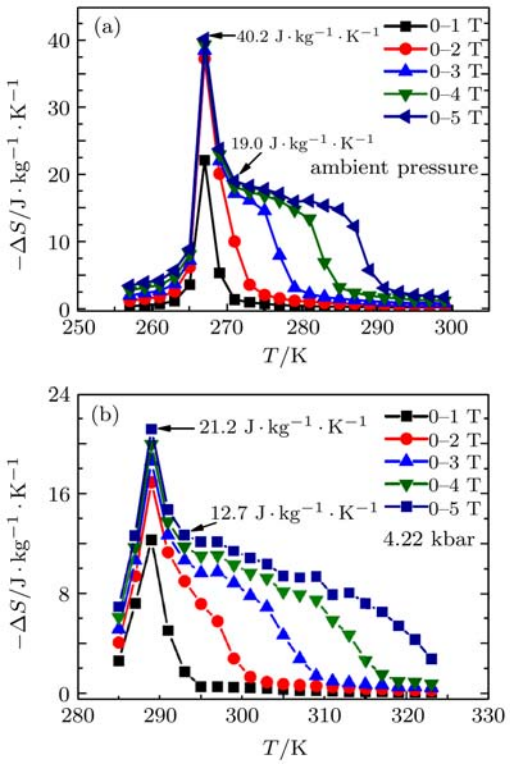



**Fig. 3.** (colour online) Temperature dependences of total entropy changes due to changes in the magnetic field at (a) ambient pressure and (b) 4.22 kbar.

of the peak, and reaches 19.0 J/kg · K at 0–5 T. The entropy change determined by the latent heat measurement is 18.9 J/kg · K,[28] which is nicely consistent with 19.0 J/kg · K of the plateau of $\Delta S$. This result also dovetails with the previous report very well.[1] It indicates that the plateau of $\Delta S$ may reflect the actual entropy change during the first-order phase transition. Compared with the results under a magnetic field, the entropy change peaks move up to the higher temperature under both a magnetic field and hydrostatic pressure, but the utmost magnitude is decreased and reaches 21.2 J/kg · K as shown in Fig. 3(b). The smooth plateau of $\Delta S$ is 12.7 J/kg · K at 0–5 T, which is a little bit larger than the previous reported result.[27] The Curie temperature is 295 K at 5 T, and 294 K at 4.22 kbar. Because the shifts of the Curie temperature are almost the same under either 5 T magnetic field or 4.22 kbar hydrostatic pressure, therefore the entropy change curve (such as the curve shown in Fig. 1(d)) can be obtained through the superimposed effect. According to Eq. (3), the entropy change at 0–5 T and 4.22 kbar is approximately equivalent to that at 0–4.22 kbar and 5 T. The entropy change at 0–5 T and 0–4.22 kbar, therefore, is obtained by superposing the curve at 0–5 T in Fig. 3(a) with that at 0–5 T and 4.22 kbar in Fig. 3(b), and shown in Fig. 4. Comparing with the results under magnetic field, the width of the entropy change curve is broadened dramatically when the hydrostatic pressure is applied at the same time. This is convincing evidence to show the large MCE and BCE in the $Gd_5Si_2Ge_2$ compound. The magnetic RC is important to evaluate the performance of the magnetocaloric materials. Here the magnetic RC is

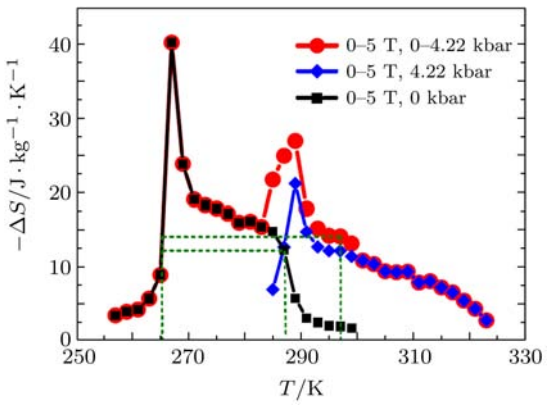



**Fig. 4.** (colour online) Temperature dependences of total entropy changes at 0–5 T and 0–4.22 kbar. The magnetic RC is 284.7 J/kg at 0–5 T (inner dashed line), and is improved to 447.0 J/kg at 0–5 T and 0–4.22 kbar (outer dashed line).

calculated in an optimum refrigeration cycle.[36,37] The results show that the magnetic RC is remarkably improved from 284.7 J/kg to 447.0 J/kg. It is obvious that a rather prominent magnetic RC can be obtained with a lower magnetic field by applying a pressure simultaneously, which is beneficial to the magnetic (or baric) refrigeration application.

## 4. Conclusion

The behavior of the first-order magnetostructural phase transition affected by magnetic field and hydrostatic pressure is analyzed theoretically and experimentally. A simple principle is proposed and employed to discuss the mechanism of the MCE and the BCE during a magneto-structural phase transition. The workable method is developed to deduce the entropy change under magnetic field and pressure, and applied to the discussion of the $Gd_5Si_2Ge_2$ compound. This method can not only reduce the strength of the required field (such as magnetic field and pressure), but also dramatically broaden the width of the entropy change curve leading to a greatly enhanced magnetic RC.

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