The magnetic and magnetocaloric properties of Gd 5 Ge 2 Si 2 compound under hydrostatic pressure

A. Magnus G. Carvalho, Cleber S. Alves, Ariana de Campos, Adelino A. Coelho, Sergio Gama, Flavio C. G. Gandra, Pedro J. von Ranke, and Nilson A. Oliveira

Articles you may be interested in

Magnetic and magnetocaloric properties of the new rare-earth–transition-metal intermetallic compound Gd3Co29Ge4B10
J. Appl. Phys. **111**, 07E333 (2012); 10.1063/1.3677658

Magnetic and magnetocaloric properties of Gd6X2Si3 (X=Ni, Co) and Ln6Co2Si3 (Ln=Pr, La)
J. Appl. Phys. **109**, 07A913 (2011); 10.1063/1.3544509

Phase relationships, and structural, magnetic, and magnetocaloric properties in the Ce 5 Si 4 – Ce 5 Ge 4 system
J. Appl. Phys. **107**, 013909 (2010); 10.1063/1.3276211

Effect of Ge substitution for Si on the anomalous magnetocaloric and magnetoresistance properties of Gd Mn 2 Si 2 compounds
J. Appl. Phys. **101**, 013908 (2007); 10.1063/1.2402975

The giant magnetocaloric effect of Gd 5 Si 1.95 Ge 2.05 enhanced by Sn doping
J. Appl. Phys. **100**, 073904 (2006); 10.1063/1.2355430

The magnetic and magnetocaloric properties of Gd$_5$Ge$_2$Si$_2$ compound under hydrostatic pressure

A. Magnus G. Carvalho
Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas—UNICAMP, Caixa Postal 6165, 13083-970 Campinas, SP, Brazil

Cleber S. Alves
CTM-DEQ-Universidade Estadual de Maringá-R. Cantor Raul Seixas, s/n-87053-240-Maringá—PR—Brazil

Ariana de Campos, Adelino A. Coelho, Sergio Gama, and Flavio C. G. Gandra
Instituto de Fisica Gleb Wataghin, Universidade Estadual de Campinas—UNICAMP, Caixa Postal 6165, 13083-970 Campinas, SP, Brazil

Pedro J. von Ranke and Nilson A. Oliveira
Instituto de Física, Universidade do Estado do Rio de Janeiro—UERJ, Rua S. Francisco Xavier, 524, 20550-013 Rio de Janeiro, RJ, Brazil

The Gd$_5$Ge$_2$Si$_2$ compound presents a giant magnetocaloric effect with transition temperature at around 276 K and is a very good candidate for application as an active regenerator material in room temperature magnetic refrigerators. Recently it has been shown that pressure induces a colossal magnetocaloric effect in MnAs, a material that presents a giant magnetocaloric effect and a strong magnetoelastic coupling, as also happens with the Gd$_5$Ge$_2$Si$_2$ compound. This motivated a search of the colossal effect in the Gd$_5$Ge$_2$Si$_2$ compound. This work reports our measurements on the magnetic properties and the magnetocaloric effect of Gd$_5$Ge$_2$Si$_2$ under hydrostatic pressures up to 9.2 kbar and as a function of temperature. Contrary to what happens with MnAs, pressure increases the Curie temperature of the compound, does not affect the saturation magnetization and decreases markedly its magnetocaloric effect. © *2005 American Institute of Physics.*
[DOI: 10.1063/1.1860932]

I. INTRODUCTION

The compounds Gd$_5$Ge$_{4-x}$Si$_x$ present the giant magnetocaloric effect (GMCE) for $1.5 \leqslant x \leqslant 2.1$ associated to a first-order magnetic transition coupled to a reversible crystallographic transition from monoclinic structure to an orthorhombic one.[1–6] As the Ge content increases the Curie temperatures (T_C) decrease from 301 K for $x=2.1$ down to 195 K for $x=1.5$, while the MCE, for a field variation of 5 T, varies from -16 J/(kg.K) for $x=2.1$ up to -46 J/(kg.K) for $x=1.5$.[5] The compound with $x=2$, Gd$_5$Ge$_2$Si$_2$, presents T_C of 272 K and a MCE of -36.4 J/(kg.K) in the optimally heat-treated condition.[5,6]

Recently, we discovered a colossal MCE in MnAs under hydrostatic pressure.[7] MnAs also presents a first-order magnetic transition coupled to a crystallographic one from hexagonal (ferromagnetic) to orthorhombic (paramagnetic), and a great magneto-elastic coupling. Pressure decreases T_C, increases the thermal hysteresis, and induces the colossal MCE for pressures up to 2.7 kbar.[7] Colossal differs from giant magnetocaloric effect by an order of magnitude greater. As the GdGeSi alloys present similar structural and magnetic behavior as MnAs, we became interested in determining if pressure can induce in it the colossal MCE. This interest was enhanced by the results of a phenomenological model developed to describe the first order phase transition in GdGeSi. The model predicts that pressure would enhance the MCE while decreasing the Curie temperature,[8] as observed for MnAs compound, though not of colossal nature.

II. EXPERIMENTAL

The Gd$_5$Ge$_2$Si$_2$ sample was prepared from 99.9 wt % Gd and with electronic grade Si and Ge by arc-melting. The resulting button was heat-treated at 1300 °C under inert atmosphere (Ar) for 1 h. The sample was characterized by x-rays diffraction, metallography and magnetic analysis. The results showed the sample containing the monoclinic phase with small additions of a second phase. The magnetic analysis confirmed the monoclinic phase with a first-order transition at 274 K when increasing temperature, and a small amount of the orthorhombic phase with a second-order transition at 298 K. Measurement of the saturation magnetization at 4 K in fields up to 7 T shows a maximum magnetic moment of 235 emu/g or 8.23 μ_B/Gd ion, in good agreement with values previously reported.[9]

The MCE measurements were done by the magnetic method, using the integrated Maxwell relation

$$\Delta S(T,H) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T} \right)_H dH. \tag{1}$$

The magnetization of the sample at different temperatures was obtained using a commercial SQUID magnetometer.

For the pressure measurements, we used a Cu–Be clamp type cell, able to work up to 12 kbar at 300 K. This cell is cylindrical and has screws in its extremities used to keep the applied pressure fixed. The sample was inserted in a Teflon container filled with mineral oil. Our pressure scale, up to 2.1
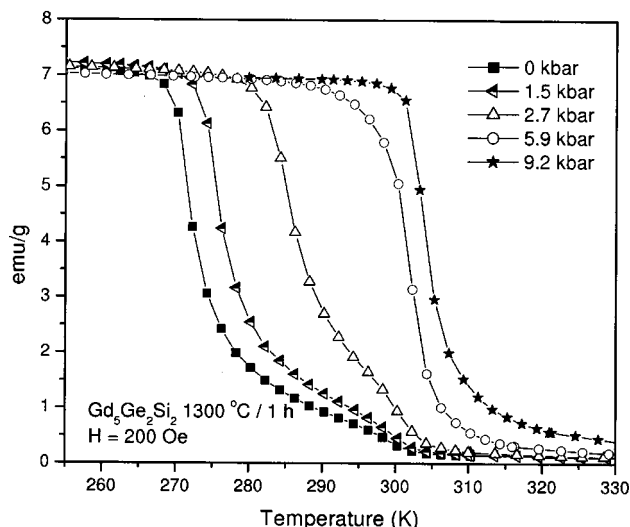
FIG. 1. Low field magnetization vs increasing temperature curves, with a rate of 1.0 K/min, for the $Gd_5Ge_2Si_2$ heat-treated sample for different applied pressures.

FIG. 3. The MCE, from magnetization vs applied field data, for the $Gd_5Ge_2Si_2$ heat-treated sample for different applied pressures.

kbar, has been obtained using a MnAs sample as a manometer, measuring T_C's determined increasing the temperature, and comparing with data from Menyuk *et al.*[10] Above this value, the pressure values were obtained by extrapolation from the calibration curve. For the MCE determination, $M \times H$ curves (up to $H = 5$ T) at several fixed pressures were taken with both field and temperature always increasing.

III. RESULTS AND DISCUSSION

Figure 1 shows the behavior of the low field magnetization as a function of temperature of the sample for different values of the applied pressure, for increasing temperatures only. Figure 2 shows the Curie temperatures, defined as the maximum slope of magnetization versus temperature curves, as a function of the applied pressure for increasing temperatures. We see that in the low pressure regime the first-order Curie temperature (T_C) almost does not change, and, beyond
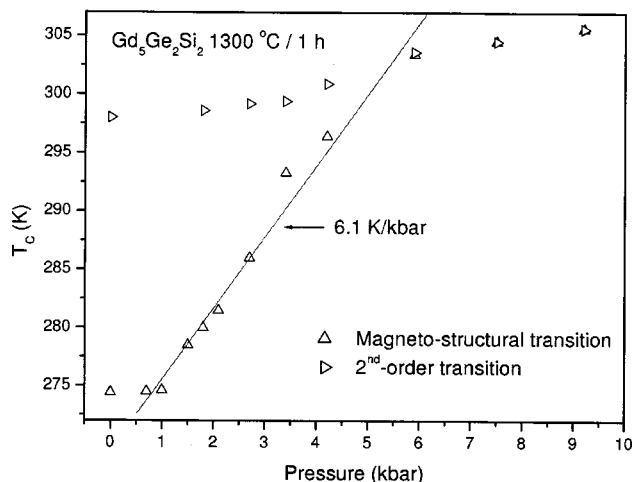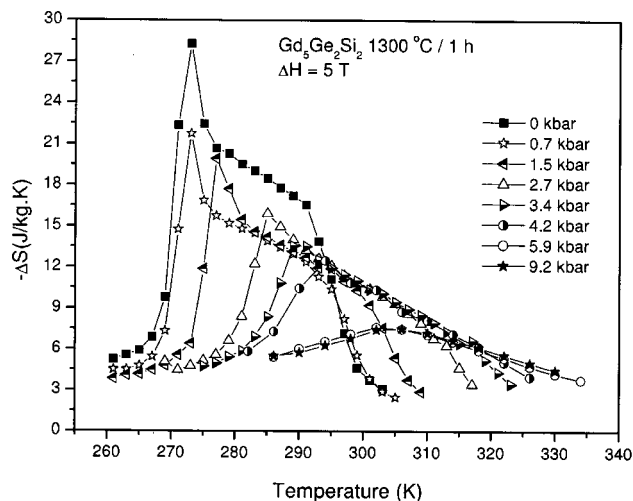

FIG. 2. Curie temperatures of the first-order and second-order transitions for $Gd_5Ge_2Si_2$ heat-treated sample as a function of applied pressure, for measurements done increasing temperature.

1.0 kbar, starts to change rapidly. Fitting the intermediate points in Fig. 2, we observe a rate of increase of T_C with pressure of $dT_C/dp = 6.1$ K/kbar. Morellon *et al.*[11] report for $Gd_5Ge_{2.2}Si_{1.8}$ the pressure-induced increase of the first-order transition temperature is linear and has a value of $dT_C/dp = 3.0$ K/kbar, lower than our measured value.

At low pressures, the behavior of the sample is very similar to the one at ambient pressure, displaying the presence of both magnetic phases, the orthorhombic phase below Curie temperature of 274 K and the monoclinic phase, above T_C. As the pressure increases, the T_C of the monoclinic phase changes to higher values, increasing the thermal hysteresis up to approximately 6 kbar, when the thermal hysteresis becomes smaller until disappearing rapidly above this pressure. The magnetic transition at 298 K is also affected by pressure and moves up to higher temperatures at a rate of $dT_C/dp \cong 0.9$ K/kbar. Morellon *et al.*[11] reported for $Gd_5Ge_{2.2}Si_{1.8}$ a value of 0.3 K/kbar, also lower than ours.

The two transitions have different rates dT_C/dp, so that at a pressure around 6 kbar the lower T_C reaches the higher one and we see only one transition after that. Remarkably, the thermal hysteresis disappears, indicating that the character of the lower transition at low pressure change from first to second order in the high pressure regime. Note that if the two transitions were persisting after this crossover, we would continue seeing two magnetic transitions displacing at different rates of their critical temperatures in this high pressure regime, but this is not observed, confirming that the two transitions merge into a second-order one.

Magnetization measurements at 4 K for pressures up to 9.2 kbar (at room temperature) and applied fields up to 7 T show that the saturation magnetization (M_S) does not change with pressure.

Figure 3 shows the measured entropic MCE under pressure for a field variation of 5 T. The ambient pressure MCE has a peak value of 28.2 J/(kg . K), typical for this compound in its preparation conditions and presenting the two ordered magnetic phases.[5,6] As pressure is increased up to 1.0 kbar, though T_C and M_S remain unaltered, there is an overall de-

crease in the values of the MCE, with the peak value changing to 21.6 J/(kg.K). As pressure is increased above 1.0 kbar the MCE curves displace to higher temperatures, and the values of the MCE decrease markedly.

We see from Fig. 3 that the peak of the $-\Delta S$ curve starts decreasing as pressure increases, and finally disappears at around 6 kbar, in which the two transitions merge. From this pressure up, the isothermal variation of entropy ($-\Delta S$) curves resemble a material presenting an ordinary (Brillouin) second-order magnetic transition, which are smooth curves.

The behavior of $Gd_5Ge_2Si_2$ under pressure is opposite the behavior of MnAs. As pressure is applied, T_C increases, while it decreases for MnAs; the thermal hysteresis first increases then decreases with pressure, while increases significantly for MnAs; the MCE increases to colossal values for MnAs,[7] while for the Gd compound the MCE decreases with the pressure. However, the magnetic behavior of both materials at ambient pressure is very similar. These differences in behavior are probably associated to the fact that $Gd_5Ge_2Si_2$ is a localized moment system, while MnAs is an itinerant compound.

IV. CONCLUSIONS

As pressure is applied, T_C of the monoclinic magnetic phase of $Gd_5Ge_2Si_2$ remains almost constant up to 1.0 kbar, and then increases up to 305 K for pressures of 9 kbar, with a rate of approximately 6.1 K/kbar in intermediate pressures. T_C of the orthorhombic phase increases with a rate of approximately 0.9 K/kbar. At around 6 kbar, the two transitions merge into a single one, which become of second order. M_S remains essentially constant up to the maximum applied pressure. The MCE effect decreases with pressure applica-

tion. As pressure increases, the peak of the MCE decreases until disappearing at around 6 kbar. From this pressure up to 9.2 kbar, the effect remains essentially constant, but showing the features of an effect associated to a second-order transition.

[1]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1977).
[2]V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Mater. (Weinheim, Ger.) **13**, 683 (2001).
[3]L. Morellon, P. A. Algarabel, M. R. Ibarra, J. Blasco, B. García-Landa, Z. Arnold, and F. Albertini, Phys. Rev. B **58**, R14721 (1998).
[4]A. del Moral, P. A. Algarabel, J. I. Arnaudas, L. Benito, M. Ciria, C. de la Fuente, B. García-Landa, M. R. Ibarra, C. Marquina, L. Morellón, and J. M. de Teresa, J. Magn. Magn. Mater. **242-245**, 788 (2002).
[5]A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Magn. Magn. Mater. **267**, 60 (2003).
[6]A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Appl. Phys. **93**, 4722 (2003).
[7]S. Gama, A. de Campos, A. Magnus G. Carvalho, A. A. Coelho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004).
[8]P. J. von Ranke, N. A. de Oliveira, and S. Gama, J. Magn. Magn. Mater. **277**, 78 (2004).
[9]V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Cryog. Eng. **43**, 1729 (1998).
[10]N. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, Phys. Rev. **177**, 942 (1969).
[11]L. Morellon, Z. Arnold, P. A. Algarabel, C. Magen, M. R. Ibarra, and Y. Skorodhod, J. Phys.: Condens. Matter **16**, 1623 (2004).