PHYSICAL REVIEW B **79**, 144430 (2009)

Magnetocaloric effect of Er_5Si_4 under hydrostatic pressure

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(Received 1 February 2009; revised manuscript received 16 March 2009; published 28 April 2009)

The magnetocaloric effect (MCE) of the compound Er_5Si_4 has been investigated as a function of the applied magnetic field (up to 50 kOe) and the hydrostatic pressure (from ambient pressure up to 9 kbar). At constant magnetic field change, increasing the pressure up to 1.4 kbar induces a global rise of the magnetic entropy change, $|\Delta S_{mag}|$, with the peak at $T_C \cong 30$ K growing from 14.9 to 20.1 J/kg K. Between 1.4 and 9 kbar, the size and shape of the $|\Delta S_{mag}|$ vs T curve remain nearly constant but the peak moves to higher temperatures and stabilizes above 3.5 kbar at $T \sim 36$ K. Contrary to many other $R_5(Si_xGe_{1-x})_4$ compounds, the magnetocaloric effect in Er_5Si_4 does not originate from the simultaneous field-induced magnetic and structural transformations since previous studies of the compound have demonstrated that moderate steady magnetic fields are not strong enough to induce the $M \rightarrow O(\mathrm{I})$ transformation at the atmospheric pressure. However, the pressure dependence of the MCE is associated with pressure-induced $M \rightarrow O(\mathrm{I})$ structural transformation that takes place in Er_5Si_4. The increase in the magnetic entropy change occurs because of a modification of the magnetic coupling derived from the differences in the interlayer bonding in the M and O(I) states. This gives rise to an enhancement of the ferromagnetic interactions in the O(I) phase with respect to the ambient pressure M state, resulting in a stronger saturation magnetization and a higher Curie temperature, i.e., $T_C^M = 30$ K and $T_C^{O(\mathrm{I})} = 36$ K.

DOI: 10.1103/PhysRevB.79.144430 PACS number(s): 75.30.Sg, 62.50.−p, 75.30.Kz, 75.25.+z

I. INTRODUCTION

The demand for advanced magnetocaloric materials that may be used in the emergent magnetic refrigeration technology requires new strategies to enhance the magnetocaloric response of the materials. In addition to the obvious quest for new compounds, many researcher groups have been concerned with doping of already known magnetocaloric alloys, modifying or improving the fabrication methods, and modifying the environmental conditions and external parameters that control the magnetocaloric effect (MCE).[1] After tuning the magnetic ordering temperature and varying the magnitude of the magnetic field, the application of hydrostatic pressure has been extraordinarily successful in the improvement of the magnetocaloric properties of several materials by increasing the magnitude and/or tuning the MCE to the desired temperature range. Some examples are $R_5(Si_xGe_{1-x})_4$ (R=rare earth),[2–4] MnAs,[5,6] $La(Fe_xSi_{1-x})_{13}$,[7] $La_xSr_{1-x}MnO_3$,[8,9] and RMn_2Ge_2.[10] However, the physical origin of the pressure effects on the MCE is not always well understood.

The $R_5(Si_xGe_{1-x})_4$ series are the best studied magnetocaloric materials since the discovery of the giant magnetocaloric effect (GMCE) in the most important member of the family, i.e., $Gd_5(Si_xGe_{1-x})_4$, with $x \cong 0.5$.[11] In this family of compounds, GMCE is found to be tunable between ∼20 and ∼295 K by varying the Si content within the composition range $0 \leq x \leq 0.5$ (and, accordingly, the Ge content between 1 and 0.5)[12] and is related to the existence of simultaneous magnetic and crystallographic phase transitions from a low-temperature ferromagnetic (FM) orthorhombic Gd_5Si_4-type state [also known as O(I), see Ref. 13 for more details about the crystallography and used notations] to a high-temperature antiferromagnetic (AFM) state with the orthorhombic Sm_5Ge_4-type structure [O(II)] in the composition range $0 < x \leq 0.3$ (Refs. 14 and 15) or to a PM phase with the $Gd_5Si_2Ge_2$-type monoclinic (M) structure when $0.4 < x \leq 0.503$.[16,17] These magnetostructural transformations and their concomitant entropy changes can be triggered by applying an external magnetic field[16] or by an external pressure,[2,3,18] giving rise to the GMCE.

Unlike the $Gd_5(Si_xGe_{1-x})_4$ alloys, the 5:4 compounds with other lanthanides do not exhibit intimate coupling of magnetism and crystallography. For instance, in $Tb_5Si_2Ge_2$ a first-order $M \rightarrow O(\mathrm{I})$ transition takes place on cooling, but long-range ferromagnetism sets within the monoclinic phase at $T_C \sim 105$ K and the $M \rightarrow O(\mathrm{I})$ structural transformation takes place at $T_t \sim 95$ K.[19] A similar but somewhat narrower gap between the magnetic ordering and structural transformations has been reported for $Tb_5Si_{2.2}Ge_{1.8}$.[20,21] As a result, the structural and magnetic transitions are no longer coupled in these systems, but the phase sequence on cooling is still the same: M-PM→M-FM→O(I)-FM. However, Morellon *et al.*[4] recently showed that the application of an external hydrostatic pressure moves the structural transformation toward higher temperature at much faster rate than the magnetic ordering transition and eventually induces a coupling of both transformations and produces a large (65%) increase in the MCE. Increasing the magnetic field also promotes the recoupling of the magnetic and phase transformations in the $Tb_5(Si_xGe_{1-x})_4$ materials.[21,22]

In the case of Er_5Si_4, the O(I) phase is not the ground state at ambient pressure. This system exhibits a O(I) crystal structure at room temperature and on cooling it undergoes a first-order $O(\mathrm{I}) \rightarrow M$ structural phase transition in the paramagnetic state at $T_t \sim 200-230$ K.[23,24] At low temperature, Er_5Si_4 becomes ferromagnetic with $T_C = 30$ K displaying no structural anomaly. However, recent investigations have demonstrated that very high magnetic fields induce the O(I) phase at low temperature (e.g., 80 kOe at 5 K).[25] In addition, hydrostatic pressure not only induces the O(I) phase at low temperature, but it also shifts the high-temperature crystallographic change at a very high rate of $dT_t/dP \sim -30$ K/kbar.[26] This causes both transitions (the high-temperature crystallographic and the low-temperature magnetic ordering) to merge and gives rise to the O(I) state over the whole temperature range. This exotic behavior of Er_5Si_4 with increasing pressure suggests that if the crystallographic transformation is shifted precisely into the range of temperatures where the magnetic ordering takes place the MCE, which has been reported to be rather moderate at ambient pressure,[26,27] may be considerably increased. We present in this work a detailed study of the effect of an external hydrostatic pressure on the magnetization and the isothermal magnetic entropy change (ΔS_{mag}) of Er_5Si_4 in magnetic fields up to 50 kOe.

II. EXPERIMENT

A polycrystalline specimen of Er_5Si_4 was synthesized by arc melting the constituent elements (the Er was prepared by the Materials Preparation Center of the Ames Laboratory[28] and was 99.86 at. % pure with respect to all other elements in the periodic table; the Si was purchased from a commercial vendor and was 99.99+wt. % pure) in a high-purity argon atmosphere. Further details on the preparation and characterization can be found elsewhere.[23,27]

A miniature CuBe pressure cell was used for magnetization measurements in a commercial (Quantum Design Ltd.) superconducting quantum interference device (SQUID) magnetometer. In this case, the pressure value is determined at low temperatures using the known pressure dependence of the critical temperature of the superconducting state of a Pb sensor placed inside the cell. The magnetization was measured under pressures up to 9 kbar (value at 5 K) in the temperature range of 5–300 K and in magnetic fields up to 50 kOe.

The magnetic entropy change ΔS_{mag} has been calculated numerically following the well-known expression:

$$\Delta S_{\mathrm{mag}}(T,H,P) = S(T,H,P) - S(T,0,P) = \int_0^H \left[\frac{\partial M(T,H,P)}{\partial T}\right]_H dH \qquad (1)$$

derived by integration of the Maxwell relation $(\partial S/\partial H)_T = (\partial M/\partial T)_H$.[29,30]

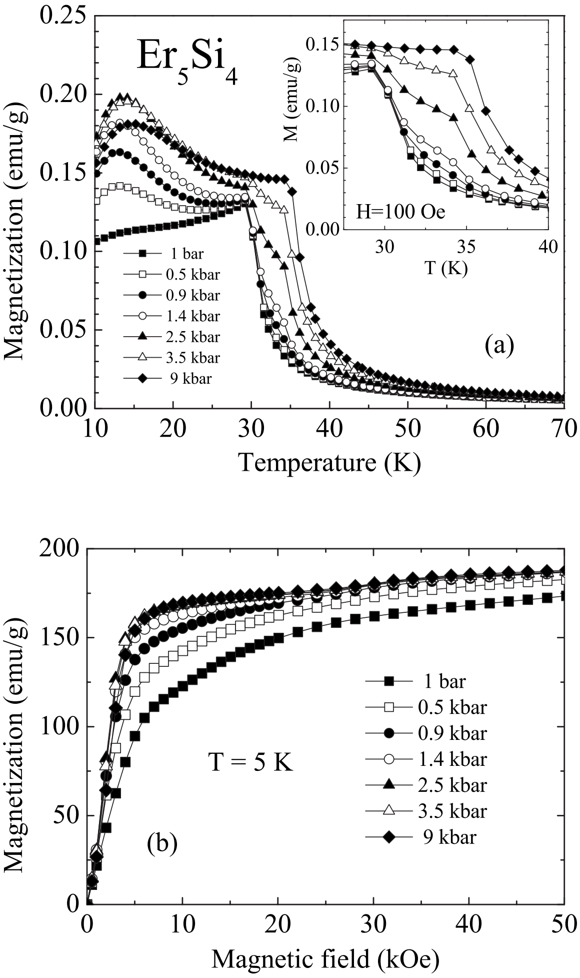

FIG. 1. (a) Temperature dependence of the magnetization of Er_5Si_4 measured in a magnetic field of 100 Oe on heating of zero-field-cooled sample as a function of hydrostatic pressure. The inset of illustrates the effect of pressure on the Curie temperature. (b) Magnetization isotherms of Er_5Si_4 measured at 5 K as a function of the hydrostatic pressure at magnetic fields up to 50 kOe.

III. RESULTS

Magnetization measurements were performed as a function of temperature, applied magnetic field, and external hydrostatic pressure focusing on the low-temperature and low-pressure regimes of Er_5Si_4, where the main changes are expected.[26] Figure 1(a) displays the temperature dependence of the magnetization of Er_5Si_4 measured on heating in a magnetic field of 100 Oe at different hydrostatic pressures ranging from 0 to 9 kbar (here and below the pressure values are quoted at 5 K). This measurement reproduces the low-field magnetization experiments under pressure already reported in a previous work.[26] The development of a broad anomaly with increasing pressure is clearly observed in the temperature range from ~10 to 20 K. This anomaly broadens continuously as pressure increases up to 9 kbar, giving rise to an overall increase in the magnetization when compared to the ambient pressure $M(T)$ data. Furthermore, the maximum of this low-temperature shoulder increases up to $P \sim 3$ kbar, decreasing afterwards.

A second process occurs within a few Kelvin above the ambient pressure Curie temperature $T_C=30$ K and is detailed in the inset of Fig. 1(a). In addition to the increasing ordering temperature, a new anomaly seen as a break in the $M(T)$ emerges progressively around 34 K with increasing pressure. Both anomalies (the broad shoulder and the break) coexist between 0.9 and 3.5 kbar; at 3.5 kbar the anomaly at $T\cong 34$ K becomes dominant. At a maximum pressure (9 kbar) there is no longer a trace of the transition at 30 K, and only the transition at 36 K remains.

Using neutron diffraction, Magen *et al.*[26] demonstrated that these changes in the low-temperature magnetization are associated with the pressure-induced first-order crystallographic transformation from the M ambient pressure state with $T_C^M=30$ K to the $O(\mathrm{I})$ high-pressure phase with the Curie temperature of $T_C^{O(\mathrm{I})}=36$ K. The onset of this transition and its evolution toward higher temperatures with increasing pressure is reflected in the magnetization by the growing break of the $M(T)$ curve at ~ 34 K. Moreover, the rising anomaly at $T\sim 36$ K reflects the higher Curie temperature of the emerging $O(\mathrm{I})$ phase, whereas the first-order character of the M-$O(\mathrm{I})$ transformation is reflected in the absence of intermediate transition temperature values. Comparing the 1 bar and the 9 kbar curves in Fig. 1, it is clear that the low-field magnetization of the high-pressure $O(\mathrm{I})$ not only reveals a higher T_C, but it also confirms that $O(\mathrm{I})$-Er_5Si_4 has a higher magnetization than the low-pressure M-Er_5Si_4 phase.

The same effect is seen in the magnetization isotherms shown in Figs. 1(b) and 2. The dependence of the magnetization isotherms at 5 K on the hydrostatic pressure is illustrated in Fig. 1(b). This experiment evidences a strong change in the shape and magnitude of the magnetization when pressure increases up to ~ 2.5 kbar after which they remain virtually unaffected by pressures between 2.5 and 9 kbar. At the maximum field, the magnetization value changes from 170 emu/g at the ambient pressure to 185 emu/g at pressures higher than 1.4 kbar—an increase of 9%. This enhancement of the magnetization is more pronounced in the magnetic fields below 20 kOe, where the magnetization slowly increases with field in the low-pressure curves, whereas the high-pressure isotherms exhibit a much more rapid tendency toward saturation. Even greater changes in the magnetization with pressure are observed in the vicinity of the Curie temperatures (not shown), where an increase of up to 30% in the magnetization at 50 kOe is seen. This is directly related to the change in the magnetic structure of Er_5Si_4 upon the $M\rightarrow O(\mathrm{I})$ transformation, as the M phase is a strongly canted FM state, but the $O(\mathrm{I})$ phase orders ferromagnetically in a nearly collinear structure with higher Er magnetic moments in low field.[25] It is worth noting that some discrepancies in the shape of $M(H)$ curves and pressure values compared to previous results are related, respectively, to texture that is always present in the as-solidified alloys and to the uncertainty in the determination of the absolute pressure values.[26]

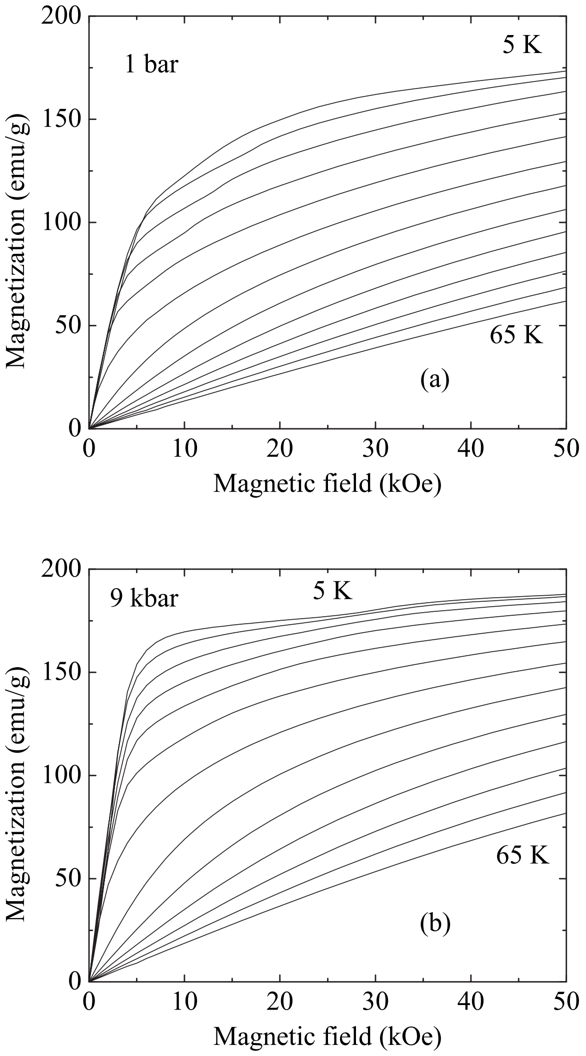

FIG. 2. Magnetization isotherms of Er_5Si_4 measured at (a) ambient pressure and (b) 9 kbar in the temperature range 5–65 K with a temperature step of $\Delta T=5$ K in magnetic fields up to 50 kOe.

Several sets of magnetization isotherms have been measured at different pressures in the temperature range from 5 to 65 K in order to calculate the magnetic entropy change. Two examples (at 1 bar and 9 kbar) are displayed in Figs. 2(a) and 2(b), respectively. The same pressure-related features as seen in Fig. 1 are also noticeable in Fig. 2. The magnetic entropy changes (ΔS_{mag}) calculated using Eq. (1) from the aforesaid magnetization isotherms are shown in Fig. 3 for two different magnetic field changes, $\Delta H=20$ kOe in Figs. 3(a) and 3(b) and $\Delta H=50$ kOe in Figs. 3(c) and 3(d). In all cases two different regimes are observed in the MCE as a function of pressure. For $\Delta H=20$ kOe, the magnitude of the MCE increases with pressure from 7.1 J/kg K at ambient pressure up to 9 J/kg K at 1.4 kbar with a peak value remaining at a constant temperature of $T\sim 30$ K, which corresponds to T_C^M [Fig. 3(a)]. Simultaneously, a broad shoulder develops at about 15 K. On the other hand, when $P>1.4$ kbar the MCE moves progressively to higher temperature and its maximum keeps increasing in its magnitude. The main peak reaches a maximum value of $\Delta S_{\max}=11.1$ J/kg K at 9 kbar and $T\sim 36$ K, which coincides with $T_C^{O(\mathrm{I})}$ [Fig. 3(b)], giving rise to a 56% enhancement of the MCE peak at the magnetic field change of 20 kOe with respect to ambient pressure. The low-temperature shoulder, on the other hand, is gradually reduced, merging with the main

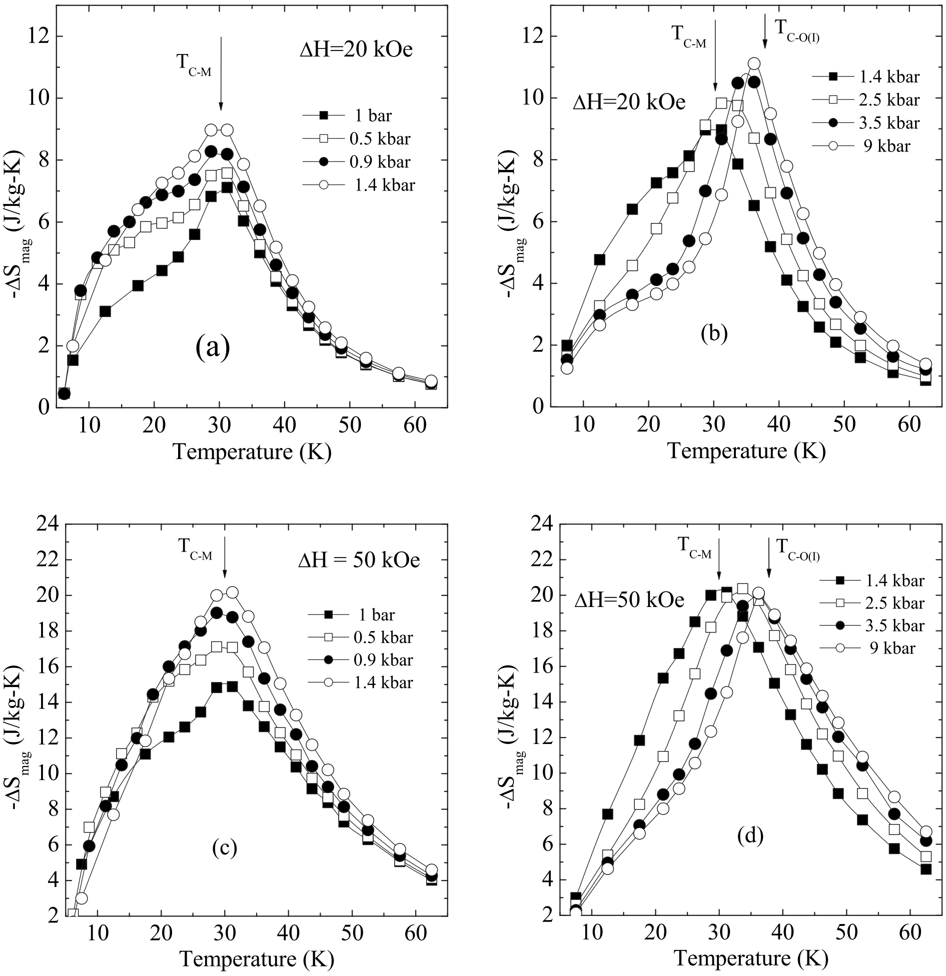

FIG. 3. Magnetocaloric effect of Er_5Si_4 for different values of magnetic field change at hydrostatic pressures: (a) $\Delta H=20$ kOe and P from 1 bar to 1.4 kbar, (b) $\Delta H=20$ kOe and P from 1.4 to 9 kbar, (c) $\Delta H=50$ kOe and P from 0 to 1.4 kbar, and (d) $\Delta H=50$ kOe and P from 1.4 to 9 kbar.

peak between 2.5 and 3.5 kbar. With a magnetic field change of 50 kOe, although the low-temperature shoulder is less pronounced than at 20 kOe in relation with the main peak, its evolution upon increasing pressure is similar and it also merges with the main peak, in this case above 1.4 kbar. However, the progression of the main peak with pressure is somewhat different. The ambient pressure MCE amounts to 14.9 J/kg K and the magnitude of the MCE peak saturates at $P\sim1.4$ kbar, with a maximum value of $\Delta S_{\mathrm{max}}=20.2$ J/kg K at T_C^M [Fig. 3(c)], an overall increase of 35%. At higher pressure, this peak value remains constant at higher pressures, but its position shifts toward higher temperatures, reaching $T_C^{O(\mathrm{I})}$ at 3.5 kbar and remaining constant so far, as can be seen in Fig. 3(d).

IV. DISCUSSION

The main features displayed by the MCE curves, the pressure dependencies of the maximum value of $|\Delta S_{\mathrm{mag}}|$ and of the temperature of the peak, are plotted in Figs. 4(a) and 4(b), respectively. As it is easy to see in Fig. 4(a), the peak value of the MCE saturates at 1.4 kbar for $\Delta H=50$ kOe, whereas at 20 kOe this saturation occurs at some pressure value between 3.5 and 9 kbar. Therefore, there is an obvious

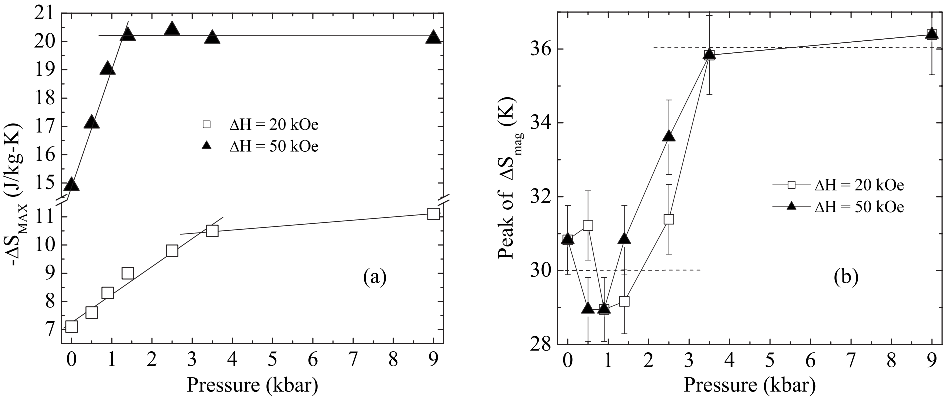

FIG. 4. (a) Maximum value of the magnetic entropy change and (b) temperature of the main MCE peak of Er_5Si_4 as a function of the magnetic field change and the hydrostatic pressure. The horizontal dashed lines mark the Curie temperatures of the M phase (lower) and the O(I) phase (higher).

relation between the magnetic field change and hydrostatic pressure needed to maximize the MCE. Taking into account the magnetostructural processes triggered by magnetic field and pressure in this system, the fact that a 50 kOe magnetic field is capable of saturating the MCE at $P \geq 1.4$ kbar points to the completion of the low-temperature M-FM $\rightarrow O$(I)-FM transformation. In other words, the combined effect of a 50 kOe magnetic field and pressures higher than 1.4 kbar promotes a rapid formation of the high-pressure–high-magnetic-field phase of Er_5Si_4, which is the O(I)-FM state. Otherwise, this is not possible to achieve a complete magnetic-structural transition at ambient pressure and moderate magnetic field (up to 50 kOe), as only a 60% of the transformation is induced and high-pulsed magnetic fields are needed to obtain a complete transition,[25] and at zero magnetic field a hydrostatic pressure of about 5 kbar is necessary to complete it.[26] We can also see this interplay between magnetic field and pressure effects in the evolution of the peak temperature displayed in Fig. 4(b). In spite of the large error bars and reduced number of points, the crossover of the peak temperature from $T_C^M = 30$ K to $T_C^{O(\mathrm{I})} = 36$ K seems to take place at a lower pressure in the 50 kOe case.

The evolution of the MCE as a function of the magnetic field and the hydrostatic pressure parallels that of the magnetization isotherms in Fig. 2. Whereas at 1 bar the magnetization at 20 kOe is far from saturation, which indicates that the M-O(I) crystallographic transformation is not induced, at 9 kbar the crystal structure is O(I) in zero magnetic field. Hence, magnetization isotherms saturate easily below 20 kOe. Relationship between the magnetic field and pressure effects can be seen in Fig. 1(b), where the effect of pressure on the magnetization saturates at about 2.5 kbar at 5 K, but the efficiency of the magnetic field in aiding in the crystallographic transformation is reduced at higher temperatures. As a result, higher pressure is needed to complete the transformation. From other experiments not shown here, we confirm that the saturation of pressure effects occurs at 15 K between 2.5 and 3.5 kbar, and at $T = 35$ K it takes place above 3.5 kbar.

Magen *et al.*[26] estimated that the O(I) state is set at all temperatures at pressures higher than ~5.5 kbar, so in all cases the value of the pressure-maximized MCE observed below 5.5 kbar depends on the applied magnetic field. Indeed, pressure is an important variable that one can use to improve the magnetocaloric performance of this material, as it is possible to lower the applied magnetic field needed for an optimal magnetic refrigeration cycle by changing the external pressure. On the other hand, if a high magnetic field is available, then the required hydrostatic pressure may be lowered.

The evolution of the magnitude and the temperature of the MCE peak underlines a new feature of the magnetocaloric properties of the Er_5Si_4 compound with respect to other members of the $R_5(Si_xGe_{1-x})_4$ family of compounds. The enhancement of magnetocaloric effect in Er_5Si_4 is due to two factors. One originates from the simultaneity of both magnetic and structural changes and the concomitance of both entropy changes induced at low pressure. The other factor is deduced from the following analysis. Above 5.5 kbar the structural transformation in Er_5Si_4 is suppressed, and the O(I) state is set for the whole temperature range.[26] However, the magnitude of the MCE saturates and remains virtually constant in the high-pressure range where no structural transition takes place. Therefore, at high pressure a second contribution to the rise of the MCE is due to the modification of the magnetic coupling derived from the differences in the interlayer bonding in the M and O(I) states.[17] This gives rise to an enhancement of the FM interactions in the O(I) phase with respect to the ambient pressure M state. As a result, the Curie temperature and the saturation magnetization of the O(I) phase are higher, and the MCE enhancement is induced by the progressive transformation due to increasing the hydrostatic pressure on the M phase and transforming it into the O(I) state assisted by the external magnetic field.

ACKNOWLEDGMENTS

C.M. would like to acknowledge the Fundación Ramón Areces for the grant “Beca para ampliación de estudios en universidades y centros de investigación en el extranjero en el campo de las Ciencias de la Naturaleza (2006-2007).” Ames Laboratory is operated by Iowa State University of Science and Technology for the (U.S.) Department of Energy under Contract No. DE-AC02-07CH11358. Work at Ames Laboratory was supported by the Office of Basic Energy Sciences, Materials Sciences Division. The authors also wish to thank A.O. Tsokol for preparing the Er_5Si_4 sample used here and in earlier[24–26] studies.

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