Pressure-Induced Colossal Magnetocaloric Effect in MnAs

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To present day, the maximum magnetocaloric effect (MCE) at room temperature for a magnetic field change of 5 T is 40 J/(kg K) for MnAs. In this Letter we present colossal MCE measurements on MnAs under pressure, reaching values up to 267 J/(kg K), far greater than the magnetic limit arising from the assumption of magnetic field independence of the lattice and electronic entropy contributions. The origin of the effect is the contribution to the entropy variation coming from the lattice through the magnetoelastic coupling.

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The MCE is the basis for the magnetic refrigeration technique [1–5]. Recently, several apparatuses for refrigeration around room temperature were disclosed, clearly showing the plausibility of such technology [6,7]. The importance of the magnetic refrigeration relies on the use of environmentally friendly materials and on greater energy efficiency. A limitation for this technology is the need of high magnetic fields to obtain large enough temperature variations. For this reason, one of the main topics on the study of the MCE is the search for materials with enhanced effects compared to the ones already known.

The MCE is significant around the magnetic phase transitions. In 1997 it was discovered that the compound $Gd_5(Ge_{1-x}Si_x)_4$, $x \leq 0.5$, presents a giant MCE (GMCE) with T_C's tuned from ~20 K($x = 0$) up to 276 K($x = 0.5$) [8–11]. This remarkable material presents simultaneously a first order magnetic transition coupled to a crystallographic one. In 2001 it was shown that the compound $LaFe_{11.4}Si_{1.6}$ also presents a GMCE [12], and later in 2003 it was announced that the compound $La(Fe_{0.88}Si_{0.12})_{13}H_y$ presents the GMCE with low values of the thermal hysteresis [13]. In 2001 two other materials were shown to present the GMCE: MnAs, with $T_C = 318$ K, and the series of compounds $MnAs_{1-x}Sb_x$, $0 < x < 0.3$ [14–16]. MnAs also presents a first order magnetic transition coupled to a crystallographic one, from hexagonal to orthorhombic structure, with a large thermal hysteresis and a GMCE that is twice the value first reported for $Gd_5Ge_2Si_2$ [8]. In 2002 it was disclosed that the compound $FeMnAs_{0.55}P_{0.45}$ also presents a GMCE with a first order magnetic transition at 300 K but with a low value for the thermal hysteresis [17,18]. Among all these materials, for a field variation of 5 T, the highest reported $-\Delta S$ is 40 J/(kg K) for MnAs [14] around room temperature.

The magnetocaloric effect corresponds to the temperature variation a magnetic body suffers when submitted to a magnetic field change. It is described by the isothermal entropy variation observed in these operations. Integration of the Maxwell relation

$$\left(\frac{\partial S(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H \qquad (1)$$

allows one to obtain the entropy variation from isothermal magnetization measurements as a function of the applied field. The Maxwell relation involves the total entropy of the body, comprising the contributions from the lattice, the electrons, and the magnetic system. For materials with localized moments it is a good approximation to take the lattice and electronic contributions as magnetic field independent, so that all the field induced isothermal entropy variation can be ascribed to the magnetic contribution to the entropy, ΔS_M. When we are dealing with itinerant magnetic materials, the assumption of field independence of the lattice and electronic contributions is only valid if the electron-phonon interaction is small [1]. The same can be said for systems showing magnetoelastic interactions. However, the field independence of the electronic and lattice terms is usually adopted in practice for all materials. Consequently, it is also usually accepted that the upper limit for the molar entropy variation is given by the magnetic contribution

$$\Delta S_M^{\max} = R \ln(2J + 1), \qquad (2)$$

even though this can be, in principle, surpassed when a system undergoes a first order transition, once the entropy variation of the system is dominated by the latent heat of the transition [1,19,20]. However, to the best of our knowledge, no GMCE material is reported as presenting an entropic MCE that reaches this limit, as can be seen from Table I.

Also, phenomenological models of the GMCE for several of the materials in Table I at ambient pressure confirm that the observed MCE's are well described using this

TABLE I. Curie temperatures, effective moments, and observed and expected $-\Delta S_M$ for materials presenting giant MCE for a field variation of 5 T around or near room temperature.

Material	Curie Temperature (K)	J or S	Observed ΔS_M^{max} [J/(kg K)]	Expected ΔS_M^{max} [J/(kg K)]	References
$Gd_5Si_2Ge_2$	272	3.5	36.4	88.9	[29]
MnAs	318	2	40	103	[14]
FeMnAsP	305	1	18	117	[17]
$MnAs_{0.9}Sb_{0.1}$	283	2	30	103	[14–16]
$La(Fe_{0.88}Si_{0.12})_{13}H_1$	274	1	23	127	[13]

approximation of magnetic field independence [21–23] of the lattice and electronic contributions to the entropy.

In Table I, MnAs is the compound in which the first order magnetic transition was first observed [24–27]. It presents a crystallographic transition from hexagonal (NiAs) to orthorhombic (MnP) structure, simultaneously with the first order magnetic transition. Its peculiar magnetic properties motivated the development of the first phenomenological model to explain the observed magnetic first order transition [25]. This motivated the study of its magnetic properties under hydrostatic pressures [27], showing a decrease of the Curie temperature as pressure increases, together a widening of the thermal hysteresis.

Recently we started the study of the magnetic properties and the magnetocaloric effect of MnAs under hydrostatic pressures. The MnAs sample was prepared from 99.99% pure Mn and 99.9999% pure As and is single phase. The sample was fully magnetically characterized, presenting a saturation magnetization (M_S) at 4 K of 3.2 $\mu_B/(\mathrm{Mn})$, $T_C = 318$ K when increasing the temperature, and 311 K when decreasing the temperature, and a maximum $-\Delta S$ of 47 J/(kg K). These values are in excellent agreement with the literature [24–27].

For the pressure measurements we used a Cu-Be clamp type cell, able to work up to 12 kbar at 300 K in our SQUID magnetometer. Our pressure scale has been obtained from the transition temperatures determined increasing the temperature, and comparing these values with the ones from Ref. [27]. For the MCE determination, $M \times H$ curves up to $H = 5$ T at several temperatures were taken with both field and temperature increasing. Near T_C a step of 1 K was adopted.

Figure 1 shows the magnetization isotherms used to calculate the MCE for a pressure of 1.80 kbar, similar for all the other measured pressures. Below T_C, the behavior is ferromagnetic, and above, we have a strong initial response of the magnetization, followed by a plateau and by a metamagnetic transition to the ferromagnetic state at a critical field. As the temperature is increased, this critical field shifts to higher values.

Figure 2 shows the measured MCE. As pressure increases, T_C decreases, following the behavior described in the literature [27]. Notably, the MCE increases very fast with pressure, reaching a maximum value of 267 J/(kg K) for 2.23 kbar. Increasing the pressure beyond this value, the effect starts to diminish, and for pressures above 2.64 kbar it shows very low values. The disappearance of the MCE is associated with a strong decrease of the saturation magnetization (M_S) with pressure, as well as the onset of a new magnetic ordering, possibly antiferromagnetism, as also described in the literature [27,28]. These maximum MCE values are far above the values predicted by Eq. (2) based on the hypothesis of magnetic field independence of the lattice and electronic contributions to the entropy, as shown in Fig. 3. From this figure we obtain that the maximum value of the entropic MCE varies with pressure at a rate of 92.4 J/(kg K kbar). We note that already for the pressure of 0.38 kbar the measured MCE surpasses the limit established by Eq. (2). The experimental values in Fig. 3 are far higher than the ones presented by MnAs at ambient pressure or presented by the other materials in Table I. Figure 4 compares some of our values for the MCE with the ones for the most representative materials in Table I. These values are also far higher than the ones

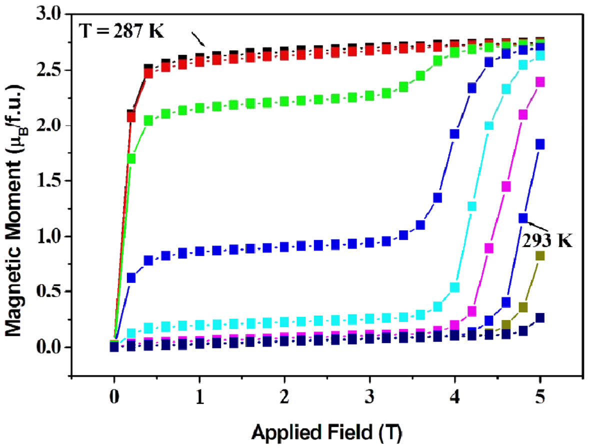

FIG. 1 (color online). Magnetization curves for as prepared MnAs at a pressure of 1.80 kbar with increasing field and temperature.

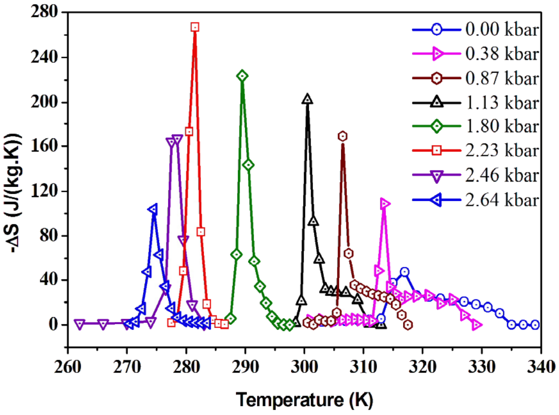

FIG. 2 (color online). The MCE as a function of temperature and pressure for as prepared MnAs.

expected from the latent heat of the first order transition, 1.79 cal/g [23.5 J/(kg K)] [25].

Examining closely Fig. 2, we observe that, as pressure increases, the shape of the MCE curve changes. For ambient and low pressures, it presents a peak followed by a plateau. As the pressure increases, the width of the plateau decreases and the peak increases very fast, until the plateau disappears. This suggests some kind of area conservation is happening here. In fact, the area of the entropy variation curve of the MCE defines the refrigerating power of the material, and has an upper limit given, even for materials presenting first order magnetic transitions, by the expression [1]

$$\int_0^\infty \Delta S dT = -M_S \Delta H \tag{3}$$

In this equation, S is the total entropy and ΔH is the field variation. As far as M_S does not change, it is to be expected this area to be constant for all pressures. The inset in Fig. 4 shows the value calculated from Eq. (3) as a dashed line and the experimental values of the areas obtained by numerical integration of the experimental curves. There is a small variation of the area as pressure increases, at a rate of 32 J/(kg kbar), but all values are below the one calculated from Eq. (3), that represents an upper limit for all the curves. We emphasize that these data are in accordance with the equation that involves the total entropy and an intrinsic property of the material, M_S. However, the maximum values of the MCE are far greater than the ones expected from the measured latent heat of the transition or from Eq. (2), obtained exclusively from the magnetic contribution to the entropy, i.e., using explicitly the assumption of magnetic field independence of the lattice and electronic contributions to the entropy.

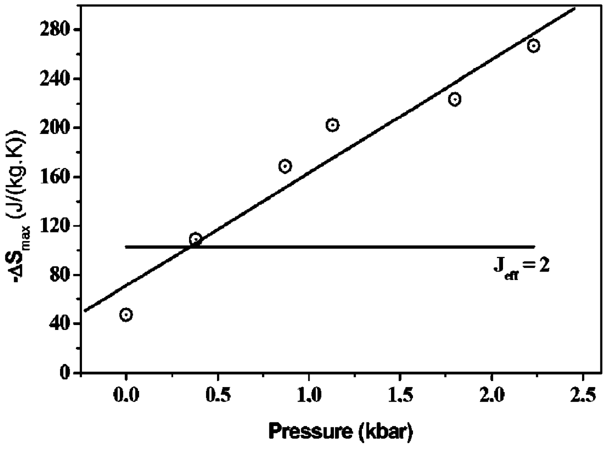

FIG. 3. Experimental maximum $-\Delta S$ values (circles) for MnAs under pressure, and comparison with the theoretical magnetic upper limit value for $J_{\rm eff} = 2$ for the Mn atom.

As the maximum values for the MCE of MnAs under pressure are so far greater than the ones observed for all the other materials up to this day, we termed the effect colossal magnetocaloric effect (CMCE). The maximum value of the entropic CMCE reaches a peak at 267 J/(kg K) for $T = 281$ K and $p = 2.23$ kbar, 7.3 times greater than the value for optimally prepared $Gd_5Si_2Ge_2$ [36.4 J/(kg K) and $T_C = 272$ K [29]], establishing a record value for the entropic variation under 5 T field variation. In molar terms, it results in a value of 34.7 J/(mol K), 1.47 times greater than the theoretical limit for holmium, 23.6 J/(mol K), the rare earth with the highest J value. Preliminary results from a phenomenological model, based on an extension of the Bean and Rodbell model [25], applied to MnAs under pressure [30] confirm that the lattice contribution can account for the experimental CMCE values. The strong magnetoelastic interaction in MnAs is the driving force for the structural and the first order magnetic transitions [24–27], and imposes a strong lattice contribution to the entropy, ex-

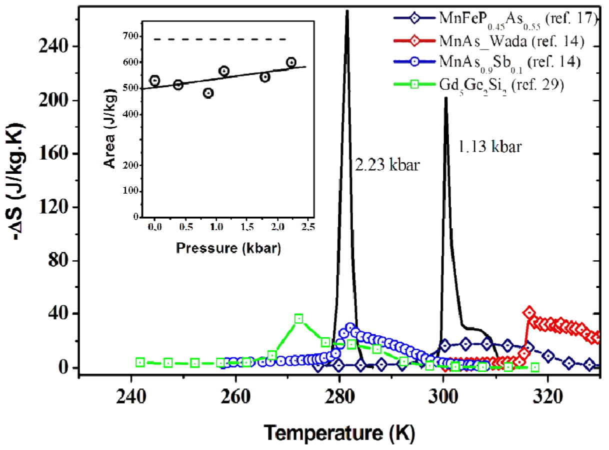

FIG. 4 (color online). Comparison of the CMCE for MnAs under pressure with MnAs [14], $MnAs_{0.9}Sb_{0.1}$ [14], $FeMnAs_{0.55}P_{0.45}$ [17], and optimally prepared $Gd_5Ge_2Si_2$ [29]. In the inset, experimental areas under the $-\Delta S$ vs T curves (circles) compared with the calculated ones (dashed line) for MnAs.

plaining the CMCE. This means that other materials presenting strong magnetoelastic interaction can also display the CMCE, as is the case of the compounds $Gd_5(Ge_{1-x}Si_x)_4$ and $FeMnAs_{1-x}P_x$.

It is tempting to think that to the colossal entropic effect corresponds a colossal temperature MCE. This is not the case, however, as demonstrated by our preliminary calculations of the total entropy curves for MnAs under pressure [30]. The calculations show that the colossal entropic effect shows up as a quasi discontinuity in both total entropy curves, presenting a small temperature separation around the transition of the order of only 8 K. (This parallels the description of the GMCE in Ref. [19].) This means that the temperature variation is relatively small, but the refrigerating power of the material is fairly great, but concentrated in a small temperature interval.

The discovery of the CMCE in MnAs is a clear experimental verification that the idea of field independence of the lattice and electronic entropy contributions to the total entropy under a field variation is not valid in general. It also highlights the possibility of a fairly large contribution from the lattice to the total entropy change of the material under a magnetic field variation, and that the available data on latent heat of the first order transition can not account for the observed colossal values measured. Without violating the sum rule, MnAs under pressure presents the highest $-\Delta S$ peak ever seen, in a narrow temperature window, and this result may be exploited in the design of new materials to work as refrigerants for magnetic refrigerators.

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