Entropy determinations and magnetocaloric parameters in systems with first-order transitions: Study of MnAs

Leticia Tocado,[a)] Elías Palacios, and Ramón Burriel

Departamento de Física de la Materia Condensada, Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

We present a study of the giant magnetocaloric effect in MnAs produced by a magnetostructural first-order phase transition. Results deduced from magnetization, M, and heat capacity, $C_{p,B}(T)$, are compared and discussed. Some spurious effects are explained, and especially a spike in the isothermal entropy change, ΔS_T, occurring at T_C when obtained via the Maxwell relation $(\partial S/\partial B)_T = (\partial M/\partial T)_B$. Alternative determination methods are given to circumvent this problem. The spike is explained as an artifact due to the incorrect application of the Maxwell relation to path dependent thermodynamic functions that are not state functions. The added wrong contribution to ΔS_T has been calculated using calorimetric data, giving a good agreement with the result from the magnetization measurements. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3093880]

Since the discovery of the so-called "giant magnetocaloric effect"[1] (GMCE) in $Gd_5Si_2Ge_2$, the magnetocaloric effect became a real alternative to the traditional refrigeration methods. Other GMCE families of compounds have been studied during the past decade, such as $MnAs_{(1-x)}Sb_x$,[2,3] $MnFeP_{1-x}As_x$,[4] $La(Fe_x,Si_{1-x})_{13}$,[5] and Ni_2MnGa.[6] In all cases the GMCE is due to a first-order structural transition in combination with magnetic ordering and changes in the electronic band structure. The entropy change is much higher than the pure magnetic contribution alone.

The characteristic parameters for a magnetocaloric compound are the adiabatic temperature increment, ΔT_S, and the isothermal entropy increment, ΔS_T, when a magnetic field $B = \mu_0 H$ is applied. Usually ΔS_T is determined from isothermal magnetization measurements by integration of the Maxwell relation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \Rightarrow \Delta S_T = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB. \quad (1)$$

This method has proven to be very useful when dealing with magnetocaloric samples undergoing second-order, purely magnetic transitions. Nevertheless, for compounds with first-order transitions the determination of ΔS_T in this way results in big errors due to the thermal hysteresis and discontinuity of M.[7] What is even worse, this method leads sometimes to unphysical results, depending on the method used to determine $M(T,B)$. Very often, a "spike" is observed at T_C in the plot of $-\Delta S_T$ versus T. A practical method for correcting this effect has been given,[8] though it has been ascribed to a failure of the Maxwell relation in the vicinity of T_C for hysteretic transitions.

In this paper we compare the results obtained from $M(T,B)$ with those from heat capacity under field $C_{p,B}(T)$ for MnAs. We explain the origin of the spurious spike and give a quantitative computation of its magnitude. MnAs presents

GMCE associated with a first-order magnetostructural transition.[2] Below $T_C = 316$ K it is ferromagnetic (F) with the hexagonal NiAs-type crystal structure. Above T_C it is paramagnetic (P) with the orthorhombic MnP-type structure. The P phase can be converted to F by an application of an external magnetic field. The magnetic phase diagram (Fig. 1) has been determined from magnetization[9] and $C_{p,B}$ measurements.[3] There is a strong hysteresis so that the transition from P to F occurs in the approximately straight line marked with open circles in Fig. 1, while the opposite transition occurs in the line of full circles. Moreover, due to inhomogeneities in composition, grain size, and defects there is a narrow interval for the transition, marked by dotted lines around the T_C values.

The simplest and most used experiment to determine ΔS_T is the measurement of several isotherms $M(T,B)$. Starting at low T and $B=0$, a series of static fields B_j is applied in increasing steps at a constant temperature T_i. When the maximum field is reached, it is lowered again down to zero. Then,
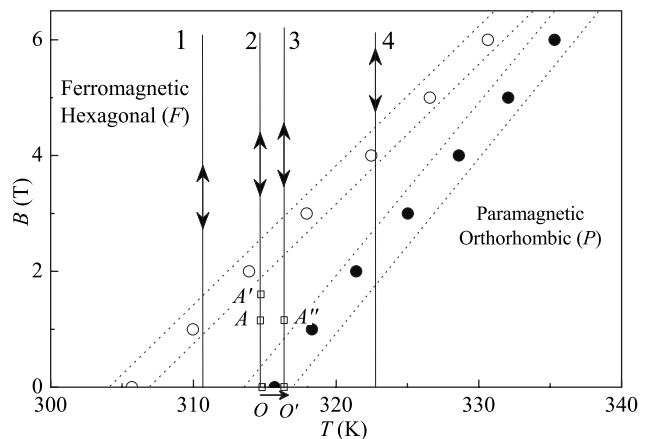

FIG. 1. Magnetic phase diagram determined from heat capacity data (Ref. 3): F to P phase transition (full circles) and P to F (empty circles). The discontinuous lines show the finite width of the phase transition bands. The vertical arrows and lines (1–4) show the paths of the magnetization measurements.
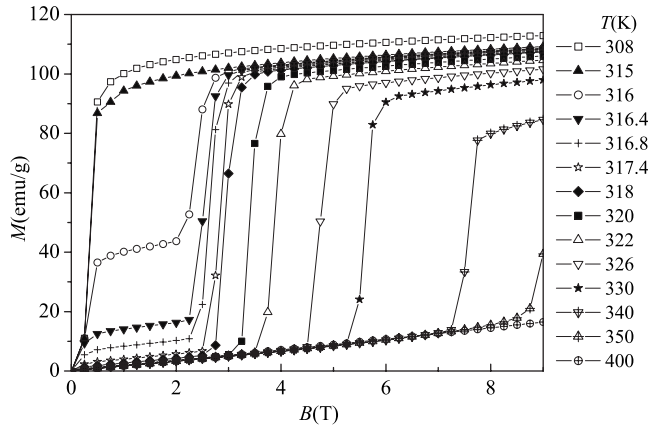
a)Electronic mail: leticiat@unizar.es.

FIG. 2. Magnetization of MnAs increasing the field at constant temperature. For the sake of clarity, only some data have been plotted.

FIG. 4. (Color online) Entropy curves of MnAs at different magnetic fields on heating by integration of $C_{p,B}(T)/T$. The discontinuous line represents the spike when ΔS_T, calculated with Eq. (2), is added to $S(T, B=6 \text{ T})$.

the sample is heated at zero field to the next temperature, T_{i+1}. Figure 2 shows some of these isotherms near T_C, measured in a physical property measurement system from Quantum Design. With these data, $(\partial M/\partial T)_B$ and the integral in Eq. (1) have been computed as

$$|\Delta S_T| = \sum_j \frac{M(T_{i+1}, B_j) - M(T_i, B_j)}{T_{i+1} - T_i} \Delta B_j. \quad (2)$$

The results are depicted in Fig. 3 for field variations from 0 to 1, 2,…, 9 T. There is a sharp spike near T_C, with a maximum $-\Delta S_{T,max} = 175$ J/kg K, sometimes referred to as a "super-GMCE," but it is nonphysical due to the experimental method. These spikes are not observed with other methods of measuring ΔS_T. From heat capacity measurements,[3] the entropy $S(T, B)$ is obtained by integration of $C_{p,B}(T)/T$. Such curves are plotted in Fig. 4. For each field the entropy increases slowly with T until the transition line (full circles in Fig. 1) is crossed horizontally, where a jump occurs. Taking the curves for $B = 0$ and for $B = 6$ T, the difference $-\Delta S_T$ increases sharply at 316 K from a small value to about 28.8 J/kg K because the zero-field entropy curve jumps at

the transition. It presents a plateau above 316 K and drops at 335 K when the curve for 6 T jumps upward to join the 0 T entropy curve. A spike in $-\Delta S_T$ at 316 K would require a similar spike in the total entropy for 0 T because $S(T, 6 \text{ T})$ is smooth at this temperature. But this is against the stability principles of thermodynamic systems requiring $(\partial S/\partial T)_B > 0$. Using the same $M(T, B)$ data, the Clapeyron equation gives similar values for the entropy jump, $\Delta S = 23$ J/kg K at T_C.

This unreal behavior can be explained considering the actual path followed in the phase diagram. At every point between the transition bands the sample can be in either phase or in a mixture of F and P phases, depending on the path followed to this point. Let x be the molar fraction of the P phase. For isotherm 1 (Fig. 1), reached from the low temperature side, $x = 0$ and Eq. (2) gives the correct results. The behavior is more complex for isotherms starting in the neighborhood of the lower transition line, such as 2 and 3. Considering a point such as A, out of the transitions bands, and two neighboring points A' and A'', the magnetization is $M = xM_P + (1-x)M_F$, and the entropy $S = xS_P + (1-x)S_F$, being M_P, M_F, S_P, and S_F the magnetization and entropy of the P and F phases, respectively. The $M(T, B)$ curves of Fig. 2 show plateaus at low fields, between the 316 and 317.4 K isotherms, due to the fraction of sample that remains in the F state.

The Maxwell relation establishes that the entropy change from A to A' can be computed from the magnetization change between A and A'' by the expression

$$\delta S \equiv S(A') - S(A) = \left(\frac{\partial M}{\partial T}\right)_B \delta B$$

$$= \frac{M(A'') - M(A)}{T(A'') - T(A)}[B(A') - B(A)]$$

$$= x[M_P(A'') - M_P(A)]\frac{B(A') - B(A)}{T_3 - T_2}$$

$$+ (1-x)[M_F(A'') - M_F(A)]\frac{B(A') - B(A)}{T_3 - T_2}. \quad (3)$$

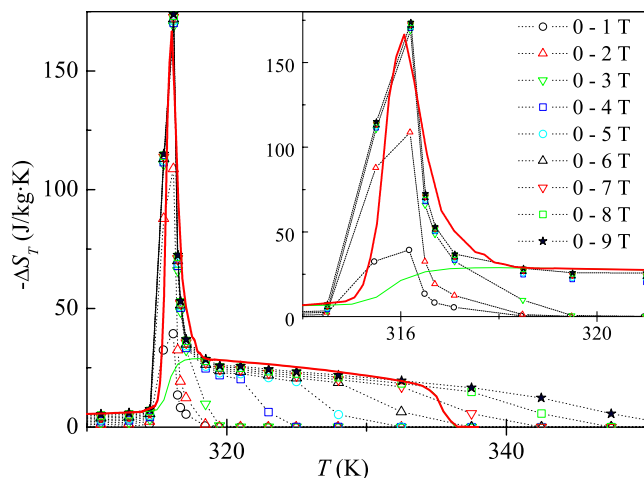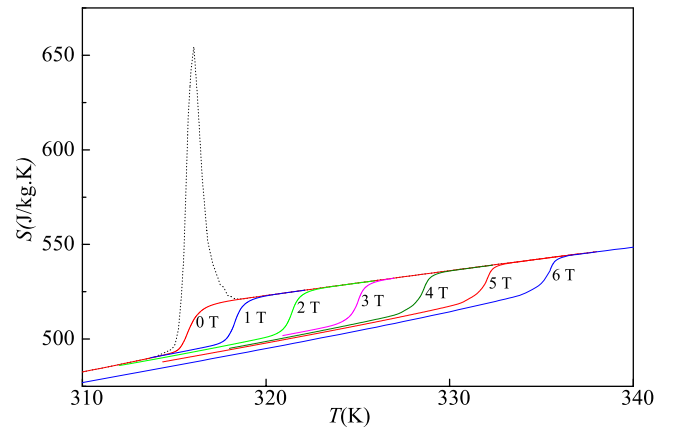This merely states that the Maxwell relation applies to each

FIG. 3. (Color online) Isothermal entropy variation in MnAs calculated from magnetization measurements with Eq. (2). The thick line shows the extra contribution derived from Eq. (6) for field $B > B_t$ added to ΔS calculated from $C_{p,B}(T)$ at 0 and 6 T (thin line).

phase, which is true out of the transition bands because x does not change on going directly from A to A' or to A''. But in the actual experiment the field is increased at constant T_2 to the maximum value and decreased again down to the point $O(T_2, B=0)$. When the state point crosses upward the upper transition band, the whole sample converts to the F state. When the field decreases, a fraction of sample x converts again to the P state in the neighborhood of $B=0$. Then, the sample is heated to the point $O'(T_3, B=0)$ at zero field, converting a portion δx to the P state.

In the calculation of the entropy increment with Eq. (2), the actual increment of magnetization from A to A'' is

$$M(A'')_{\text{exp}} - M(A)_{\text{exp}}$$

$$= \frac{\partial M}{\partial x}\delta x + \frac{\partial M}{\partial T}\delta T = [M_P(A) - M_F(A)]\delta x$$

$$+ \left[x\left(\frac{\partial M_P}{\partial T}\right)_B + (1-x)\left(\frac{\partial M_F}{\partial T}\right)_B \right](T_3 - T_2). \quad (4)$$

The second term on the right hand side gives δS as shown in Eq. (3), that is, the correct entropy increment from A to A'. The first term is due to the phase conversion from O to O', giving an extra contribution.

The value δx can be obtained from heat capacity data at zero field.[3] The integral of the anomalous $C_{p,\text{an}}$ gives the enthalpy difference or latent heat $L = H_P - H_F$ at zero field. Experimentally, the fraction of phase converted for a small increment of temperature $\delta T = T_3 - T_2$ is $\delta x = C_{p,\text{an}}(T)\delta T/L$. Substituting in Eq. (4) and introducing this extra term for the calculation of the entropy

$$\delta S_{\text{ex}} = -\frac{C_{p,\text{an}}(T)}{L}[M_F(A) - M_P(A)]\delta B. \quad (5)$$

The only variable in the field integration, $M_F - M_P$, is approximately constant until the field reaches the upper transition line, $B_t(T)$. For $B > B_t$, $x=0$, $\delta x=0$, and the extra term vanishes. The integral of δS_{ex} is

$$\Delta S_{\text{ex}} \cong -\frac{C_{p,\text{an}}(T)}{L}[M_F(A) - M_P(A)]B \quad \text{for } B < B_t,$$

$$\Delta S_{\text{ex}} \cong -\frac{C_{p,\text{an}}(T)}{L}[M_F(A) - M_P(A)]B_t \quad \text{for } B > B_t. \quad (6)$$

The shape of this extra contribution is the same as the anomalous heat capacity at zero field, $C_{p,\text{an}}(T)$. The magnitude is proportional to the field until B reaches the threshold value B_t, from where it becomes constant. For instance, the experimental maximum at 316 K is $C_{p,\text{an}} = 4800$ J/kg K and $L = 7730$ J/kg. From Figs. 1 and 2, $M_F - M_P \cong 85$ emu/g

and $B_t = 2.5$ T. This makes $\Delta S_{\text{ex,max}} = 131$ J/kg K for a field increment from 0 to $B_t = 2.5$ T or higher. $\Delta S_{T,\text{max}}$ computed via Eq. (2) is 175 J/kg K, and the value deduced from the cooling entropy curves is 27 J/kg K for a field change from 0 to 6 T. That makes a difference of 148 J/kg K, similar to the calculated $\Delta S_{\text{ex,max}}$. ΔS_{ex} has been computed using the experimental $M_F - M_P$ values for each temperature. The total value, $\Delta S_T = \Delta S + \Delta S_{\text{ex}}$, with ΔS taken from Fig. 4, is plotted in Fig. 3 and gives a remarkable good agreement with the values obtained using Eq. (2). It is also clear that the height of the spike does not increase when the field exceeds $B_t = 2.5$ T.

Care must be taken when using magnetization data to deduce the isothermal entropy change in first-order transitions. The application of the Maxwell relations to the path dependent metastable functions M and S can produce huge errors and nonphysical results for ΔS_T. A solution is to measure M, as a function of temperature, at constant fields. In this way the state points between the two transition bands are always P if the experiment is done on cooling or always F if it is done on heating. Brück[10] suggested to measure isotherms of M but heating well above T_C at zero field before cooling again down to a new temperature, which also avoids the extra contribution, ΔS_{ex}. We have calculated in MnAs the shape of the erroneous spike produced with the typical magnetization isotherms. The extra term ΔS_{ex} comes from the phase transformation that occurs at zero field upon the temperature change in the neighborhood of the transition temperature.

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