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## The La(Fe,Mn,Si)<sub>13</sub>H<sub>z</sub> Magnetic Phase Transition Under Pressure

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We study the magnetocaloric metamagnetic transition in LaFe<sub>11.74</sub>Mn<sub>0.06</sub>Si<sub>1.20</sub> and

LaFe<sub>11.76</sub>Mn<sub>0.06</sub>Si<sub>1.18</sub>H<sub>1.65</sub> under hydrostatic pressure up to 1.2 GPa. For both compounds,

hydrostatic pressure depresses the zero field critical temperature. However, in detail, pressure

influences the magnetic properties in different ways in the two compounds. In the

dehydrogenated case the transition broadens under pressure whereas in the hydrogenated case

the transition sharpens. In both cases thermal hysteresis increases under pressure, although

with different trends. These observations suggest both intrinsic and extrinsic hysteresis loss

brought about by the use of hydrostatic pressure. We explore the multicaloric field-pressure

cycle, demonstrating that although the gain introduced by overcoming the magnetic hysteresis

loss is closely countered by the loss introduced in the pressure cycle, there are significant

advantages in that the temperature range of operation can be finely tuned and extended, and

the magnetocaloric transition can operate in lower absolute applied fields ( $< 0.5$  T), potentially overcoming one of the most significant bottlenecks to the commercialization of this technology.

## **Introduction**

Magnetocaloric materials undergo a thermal response when subjected to a change in the external applied magnetic field, and those with a significant response around room temperature are considered promising for magnetic cooling applications.<sup>[1]</sup> First order phase transition  $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_{1.65}$  alloys are one such system, presenting an itinerant-electron metamagnetic (IEM) transition above the zero field Curie temperature,  $T_C$ , and significant associated isostructural volume change as a result of magnetoelastic coupling.<sup>[2-5]</sup>

Recently, the magnetocaloric properties of an engineered set of  $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_{1.65}$  were studied showing the detrimental influence of thermal and magnetic hysteresis on the refrigeration cycle,<sup>[6]</sup> and the influence of Mn and H on the strength of the first order character of the transition.<sup>[7]</sup> Strongly first order materials offer attractive properties in terms of the magnitude of entropy and adiabatic temperature but the associated thermal and magnetic hysteresis is unattractive. Recently it has been proposed to use hydrostatic pressure to manipulate the hysteresis in the magnetocaloric cycle of shape memory alloys,<sup>[8]</sup> and one aspect of the current study is to examine the relevance of this method for strongly first-order  $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_z$  in light of previous work this area.<sup>[2,9-11]</sup> A first order magnetic transition is formally defined as a discontinuous change in the first derivative of the free energy with respect to magnetic field or temperature and usually associated with measurable hysteresis related to superheating or cooling, due to latent heat of transformation. Typically for magnetocaloric first-order materials, a coupled magnetovolume or magnetostructural transition exists. Second order or continuous transitions are defined as a discontinuous change

in the second derivative of the free energy, in this case heat capacity, or magnetic susceptibility with respect to temperature or magnetic field. In this case there is an absence of hysteresis and characteristically broad magnetic transitions. In the current study, we examine the subtle changes to the character of the transition under pressure for both  $\text{LaFe}_{11.74}\text{Mn}_{0.06}\text{Si}_{1.20}$  and  $\text{LaFe}_{11.76}\text{Mn}_{0.06}\text{Si}_{1.18}\text{H}_{1.65}$ , which are referred to as dehydrogenated and hydrogenated respectively. Previously we have measured the latent heat of these compounds at the transition and at zero applied pressure directly;<sup>[7]</sup> the dehydrogenated compound presents a significantly larger latent heat contribution to the total entropy change and is assigned as having a more strongly first order transition.

## **Experimental**

The samples were synthesized by a powder metallurgical process:<sup>[12]</sup> master alloys were prepared by vacuum induction melting followed by mechanical milling steps to produce fine powders. The composition of each alloy was adjusted by blending master alloys with elemental powders. Compaction of the powder blends was performed by cold isostatic pressing. The green bodies were vacuum sintered at around 1373 K followed by an annealing treatment at 1323 K. Hydrogenation was performed on a granulate material with a particle size less than 1 mm by heating to 773 K in argon. At 773 K argon was replaced with hydrogen followed by a slow cool to room temperature.<sup>[13]</sup> The magnetization was measured using vibrating sample magnetometry (VSM) in a Quantum Design Physical Properties Measurement System. The pressure was applied by compressing a Teflon capsule, containing multiple pieces of the compound of the order of 0.5 to 1 mm in size, in a two-piston Cu-Be pressure cell filled with Daphne 7373 as the pressure-transmitting medium. The pressure was determined by measuring the superconducting critical temperature shift using VSM of a sample of pure Pb, included in the pressure cell. Measured pressure values have been adjusted to the Curie temperature at each pressure, close to which the majority of

measurements in this work are conducted, using a correction formula appropriate for this medium reported in Ref. [14] and Ref. [15]. The samples were cycled magnetically through the metamagnetic transition at ambient pressure prior to measuring in order to avoid cracking ‘virgin effects’, which are witnessed in many of these first order magnetocaloric metamagnetic systems upon first-cycling, occurring during measuring.<sup>[16]</sup> Isofield measurements were performed at a temperature rate of  $|dT/dt| = 0.5 \text{ K min}^{-1}$  while isothermal ones were performed at  $1.7 \text{ mT s}^{-1}$ . The transition fields were found for each  $M(H)$  isotherm by fitting an arctangent function and finding the temperature or field that yields the maximum derivative in the fitted curve, i.e. finding the mid-point.

## Results and Discussion

The transition temperature is depressed significantly with pressure: for the hydrogenated sample  $dT_C/dp = -71 \pm 5 \text{ K GPa}^{-1}$ , while for the dehydrogenated sample the value is practically double at  $-139 \pm 20 \text{ K GPa}^{-1}$ . It is thought that the presence of interstitial H may change the mechanical properties, such as the compressibility of the material, resulting in different responses for hydrogenated and dehydrogenated materials, while alternatively it is thought that the strength of the magnetovolume coupling may also play a role.<sup>[2,9]</sup> Recent calculations suggest a difference in absolute compressibility between hydrogenated and dehydrogenated compositions of less than 10%,<sup>[17]</sup> suggesting that the strength of the magnetovolume coupling is the dominant factor.

The heating and cooling procedures (**Figure 1(a)**) show that pressure enhances the thermal hysteresis in both compositions and as previously discussed, the magnetization decreases with increasing pressure.<sup>[9,11]</sup> For magnetocaloric performance, one of the important parameters is the magnetic entropy change ( $\Delta S_m$ ) in applied field. The results summarized in **Figure 1(b)** show  $\Delta S_m$  as a function of temperature and field, calculated using a numerical approximation

to the Maxwell relation from isothermal magnetization measurements (shown in the Supporting Information). As one can observe, pressure decreases and broadens the  $\Delta S_m$  peak for the dehydrogenated sample. We see that the magnetic entropy change of the hydrogenated sample increases initially with pressure, before decreasing at the highest pressure measured. A falling entropy change can result from application of insufficient magnetic field to complete the transition. In the hydrogenated sample case, the decrease in the  $\Delta S_m$  peak is in part due to the significant broadening of the  $M(H)$  transition (see Supplementary Data) such that the transition does not complete within the maximum applied field ranges at the higher pressures; however, for the dehydrogenated sample this is not the case, the field is sufficient to complete the transition, and the drop in the  $\Delta S_m$  peak relates to the broadening of the transition in temperature as observed in the magnetization (Figure 1(a)). Although this change in the width of the transition Figure 2(d) is subtle, it suggests different trends for the two samples. Results in the literature are conflicting as to whether pressure makes the transition in this material family more strongly or more weakly first order,<sup>[2,9,10]</sup> with discussion based on microstructure and sample shape,<sup>[16,18,19]</sup> however similar behavior to Figure 1 is found by Yamada and Sadakuni with the trends explained within the framework of spin fluctuation theory as intrinsic properties of the material.<sup>[20,21]</sup>

From the isothermal magnetization measurements, we also extract the transition fields ( $H_C$ ) at each temperature in order to analyse the  $T-H_C$  phase diagram for the different pressures, as shown in **Figure 2**(a) for the dehydrogenated sample, while (b) and (c) show  $dT_C/dH$  as a function of pressure and the thermal hysteresis at zero field, respectively, extracted from this data for both samples.  $|dT_C/dH|$  increases significantly for the dehydrogenated sample while it shows a minor decrease for the hydrogenated one. From the Clapeyron equation, which gives the purely first-order contribution to the entropy change, we have:

$$\Delta S = -\Delta M \left( \frac{dT_C}{dH} \right)^{-1} \quad (1)$$

We can see that if  $dT_C/dH$  increases with pressure, the first-order contribution of the transition to the entropy change decreases, as  $\Delta M$  is only weakly affected by pressure. This suggests that the hydrostatic pressure makes the transition less strongly first-order in the case of the dehydrogenated sample, and the opposite for the hydrogenated sample. Consistent with this, thermal hysteresis increases with pressure systematically for the hydrogenated sample, and plateaus for the dehydrogenated (a point we will come back to). However, the trend of  $dT_C/dH$  alone is not a reliable indicator of the strength of the transition.

It is important to recognize that all pressure-induced measurements of the hydrogenated sample are within the liquid state of the pressure-transmitting medium Daphne 7373 ( $T > 240$  K) whereas those for the dehydrogenated sample are in the solid state ( $T < 180$  K). However, significant deviations from hydrostaticity in the low temperature solid state, which may result in an observed broadening of the phase transition due to variations of local pressure, are not expected in this pressure range.<sup>[22]</sup> We observe a strong correlation between the transition broadening (Figure 2(d)) and the trend of  $dT_C/dH$  (Figure 2(b)) for both compounds, supporting the premise that the decrease of the strength of the first-order character with pressure when the compound is dehydrogenated, and a small increase of first-order strength with pressure for the hydrogenated, are intrinsic properties and not an artefact due to variations in hydrostaticity in the two cases. These results are consistent with the  $\Delta S_m$  behavior.

A widely accepted scenario is where hysteresis reflects the energy barrier between the stable magnetic phases in the free energy description of a first order transition, and increased hysteresis reflects an increase in height or the energy barrier for a given family of

materials.<sup>[19,23,24]</sup> However, for the dehydrogenated sample we observe contradictory behavior: an increase in  $dT_C/dH$  and transition width, and a decrease in the magnitude of  $\Delta S$  with increasing  $p$ , indicative of a weakening of the first-order character. However this is accompanied by a mostly constant discontinuous change in  $M$  in addition to an increase in thermal hysteresis, as shown in Figure 2(c) and also observed by Lyubina *et al.*<sup>[9]</sup> Interpreting these results are not straightforward as features reminiscent of both weakening and in contrast strengthening first-order behavior are observed. We speculate that the hysteresis increase is due to an extrinsic dominant contribution, caused by an additional energy barrier to phase transformation introduced by the external pressure, inhibiting magnetovolume expansion. The hydrogenated sample case is more straightforward: both the increase of first-order character and extrinsic hysteresis from pressure act together to increase the hysteresis.

The hysteresis involved in the isothermal cycle of magnetization can be interpreted as energy lost to the environment. It may be calculated at a given temperature by the area under the isothermal magnetization curve, represented by the grey shaded areas in **Figure 3(a)** for the dehydrogenated sample. This graph shows the magnetization as a function of the applied field at 175 K for two different pressures, 0 and 0.02 GPa. Additionally, it shows the difference between the first run at 0 GPa (blue line) and the final one (black line) back at 0 GPa after all the different pressure measurements. One may see in the circled areas that an irreversible step-like behavior is present after the pressure measurements. This we believe is related to cracking of the sample, as shown elsewhere,<sup>[16]</sup> whether due to virgin effects or pressure and magnetic cycling.<sup>[25,26]</sup>

Planes *et al.* show that the total entropy change for a two-step multicaloric cycle can be written as:<sup>[27]</sup>

$$\Delta S[T, (0,0) \rightarrow (H, p)] = \Delta S[T, (0,0) \rightarrow (H, 0)] + \Delta S[T, (0,0) \rightarrow (0, p)] + \int_0^H \int_0^p \frac{\partial \chi_{12}}{\partial T} dp dH \quad (2)$$

where the last term accounts for the interplay between the two caloric properties and is non-zero for any interdependent multicaloric effects, in this case the magnetovolume coupling.

Stern-Taulats *et al.* demonstrate that if we assume no change in magnetization or material compressibility with pressure at the maximum or zero field positions (where in our cycle the pressure changing steps take place), the energy loss in a field-pressure full multicaloric cycle can be approximated as  $\Delta p \Delta V$ . In this case the cross-susceptibility  $\chi_{12}$  terms represent the contribution from the change in  $M$  due to  $p$  and the change in  $V$  due to  $H$ .<sup>[28]</sup> If a multicaloric cycle is executed as follows: (1) apply the magnetic field in 0 GPa, (2) increase the pressure to 0.02 GPa, (3) remove the magnetic field in 0.02 GPa, (4) return the pressure to zero, we observe a greatly decreased magnetic hysteresis indicated by the striped areas in Figure 3(a), as has been demonstrated previously.<sup>[8,28,29]</sup> We estimate the energy losses due to the pressure-volume steps for the dehydrogenated material, with density  $7100 \text{ kg m}^{-3}$  and a volume change of 1.35% (as calculated from x-ray diffraction measurements), to be  $38 \text{ J kg}^{-1}$ . It should be noted this is an estimate, since we observe a small decrease of  $M$  after  $p$  is increased in the high field/ferromagnetic state, the magnetic hysteresis is not completely removed, and preliminary calculations of the compressibility of the parent  $\text{LaFe}_{13-x}\text{Si}_x(-\text{H}_{1.5})$  compounds with  $x=1.5$  suggest a decrease of between 8% (dehydrogenated) and 17% (hydrogenated) between the paramagnetic and ferromagnetic states.<sup>[17]</sup>

The inset to Figure 3(b) shows the net magnetic hysteresis energy involved in the isothermal cycle. The estimated figure of energy loss from the pressure-volume addition to the cycle suggests that the work done in the multicaloric cycle is approximately matched by the loss introduced in the pressure cycle, as previously reported, the precise gain or loss being material system and cycle specific.

However there are other advantages to considering the multicaloric cycle. (1) The increase in the peak entropy change under pressures up to 0.59 GPa in the hydrogenated compound provides an increased cooling power.<sup>[30]</sup> (2) The cycle shown in Figure 3(b) requires an operating field  $<0.5T$ , which could in principle be provided by inexpensive ferrite based magnets. It is important to note that for field removal at zero pressure the composition remains ferromagnetic, therefore the 0.02 GPa step here is required to complete the magnetocaloric cycle. Since for one composition this will only apply over a narrow temperature range, a set of materials with cascaded  $T_C$  would still have to be engineered to operate in the same low pressure (cascaded  $T_C$ s are currently employed in prototype refrigerators with first order materials). This would provide maximal entropy change requiring low magnetic field and operation across a wide temperature range. This addresses one of the major bottlenecks to the uptake of the technology: the need to reduce expensive rare-earth element based permanent magnets. (3) Resolving issues of working temperature in magnetic refrigerators: literature has shown that the cooling power of a magnetic regenerator may decrease by about 90% if  $T_C$  of the material is just a few kelvins from the absolute working temperature,<sup>[31]</sup> which can vary significantly during one day. Therefore, controlling  $T_C$  is of extreme relevance for application and application of pressure to fine tune performance maxima would lead to an extension of the working fridge temperature range.

## Conclusions

In summary, we have examined the influence of hydrostatic pressure on strongly first order  $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_z$  for  $z=0$  and 1.65. We find differences in the magnetic performance in samples with and without hydrogenation and evidence suggests that these differences are intrinsic. We demonstrate that in the  $\text{La}(\text{Fe},\text{Si})_{13}$  material family that we have studied the reduction of magnetic hysteresis within the thermodynamic refrigeration cycle is closely

matched by the work done in the pressure cycle. However the most important message is that by incorporating a multicaloric cycle, not only can the temperature range of operation be extended but also the refrigeration cycle can be operated in lower absolute applied fields, removing the reliance of the technology on expensive rare earth based magnets. .

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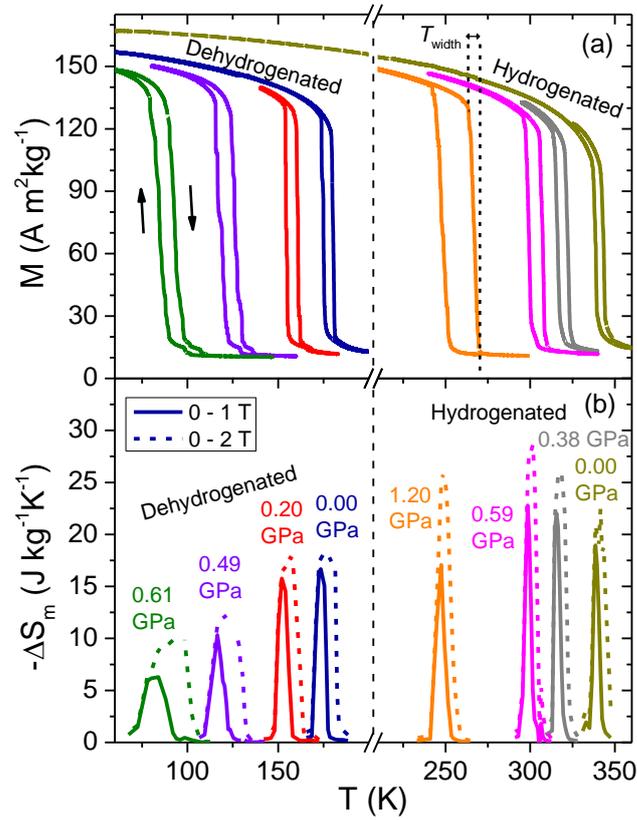
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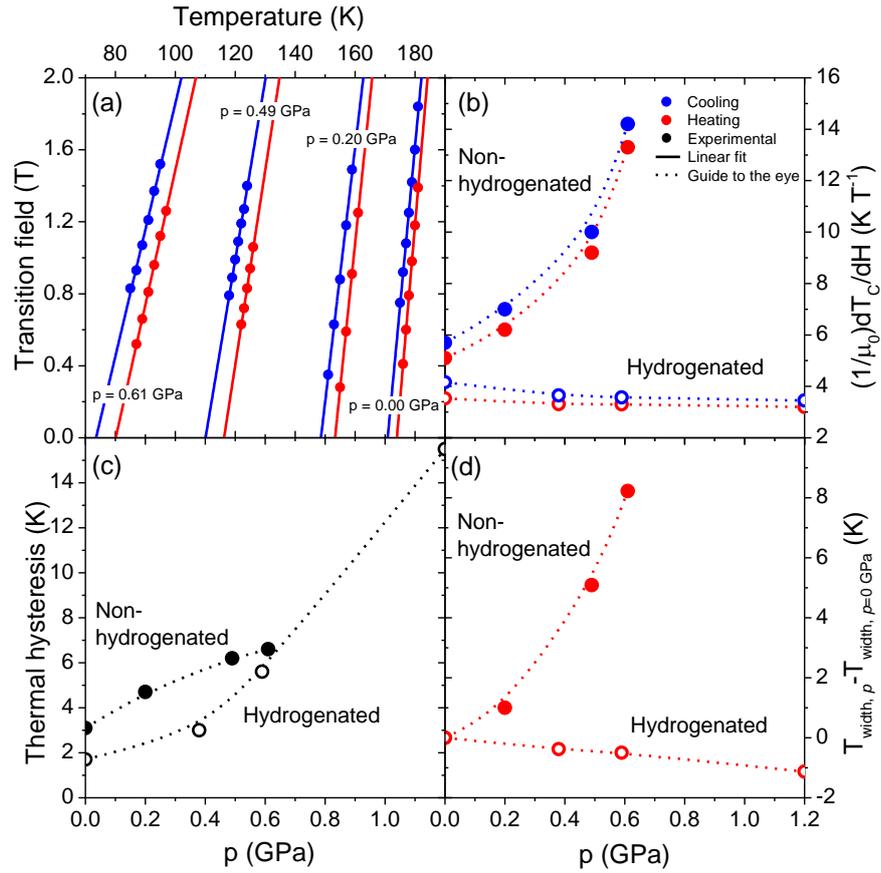
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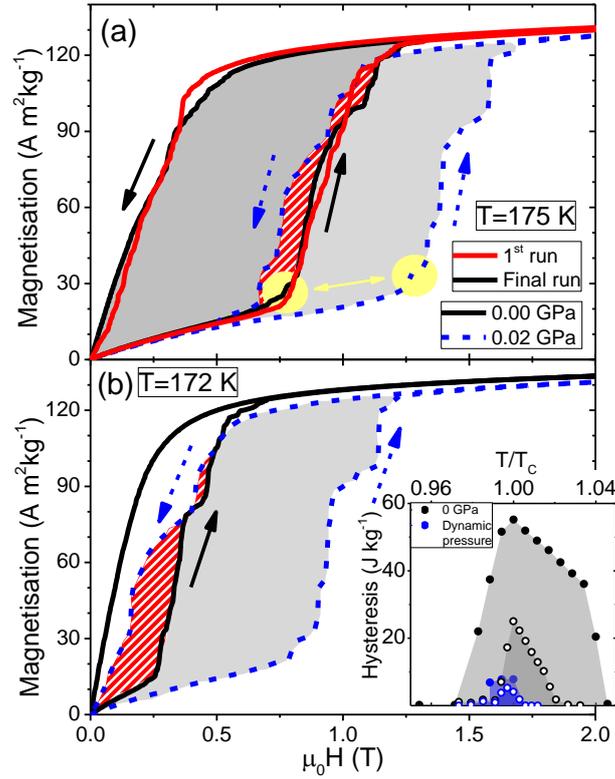
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**Figure 1.** (a) Magnetization as a function of the temperature at 1.0 T for both heating and cooling procedures and in different pressures. The estimation of the transition width is indicated by the dashed lines. (b) Magnetic entropy change  $\Delta S_m$ , during the para- to ferromagnetic phase transition for the different pressures and two different field changes.



**Figure 2.** (a) Transition temperature and field during heating and cooling for the dehydrogenated sample, (b)  $dT_c/dH$  as a function of pressure for both the heating and cooling procedures for both dehydrogenated and hydrogenated samples, (c) thermal hysteresis at 0 T as a function of pressure and (d) the change in transition width on heating in 1 T (defined as shown in Figure 1(a)) with pressure compared with the width at 0 GPa.



**Figure 3.** (a) Magnetization of the dehydrogenated compound as a function of field at 175 K for zero pressure and an applied pressure, 0.02 GPa. The solid red and black lines represents the zero-pressure measurements prior and post application of pressure, respectively. The red and white-striped area indicates the reduced magnetic hysteresis in the ‘dynamic pressure’ multicaloric cycle; grey areas represent the magnetic hysteresis at each pressure. (b)  $M(H)$  for the same sample and pressure as (a) at 172 K. Note that the field decreasing step in zero pressure (no arrow in (b)) remains in the ferromagnetic state. Inset: Net magnetic hysteresis energy (loss) in isothermal cycles as a function of the normalized temperature,  $T/T_C$ , for dehydrogenated (closed symbols) and hydrogenated (open) under zero pressure and a dynamic pressure cycle as described in (a), for 0 to 2 T. The multicaloric cycle for the hydrogenated compound is 0 GPa for increasing field and 0.01 GPa for decreasing field.