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Contributions to the Entropy Change in Melt-spun $\text{LaFe}_{11.6}\text{Si}_{1.4}$

K Morrison¹, J Lyubina², JD Moore¹, AD Caplin¹, KG Sandeman¹, O Gutfleisch² & LF Cohen¹

¹*The Blackett Laboratory, Imperial College, London SW7 2BZ, UK*

²*IFW Dresden, PO Box 260016, D-01171 Dresden, Germany*

Abstract

Here we study the calorimetric and magnetic behaviour of melt-spun $\text{LaFe}_{11.6}\text{Si}_{1.4}$, a potential magnetic refrigerant material system that exhibits the rare combination of a large entropy change and low thermal and magnetic field hysteresis. We are able to separate the calorimetric contribution from latent heat and changes in equilibrium heat capacity explicitly by using two separate calorimetric probes. The heat capacity of this sample exhibits significant changes of the order of $500\text{-}1000\text{J K}^{-1}\text{kg}^{-1}$ in response to magnetic field that results in large changes in entropy. The different contributions to entropy change from latent heat and heat capacity are shown to evolve as the material is field driven through its itinerant metamagnetic transition. We demonstrate explicitly that in the melt spun sample studied here, the majority of the total entropy change comes from the equilibrium change of heat capacity.

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1. Introduction

Systems that show a large magnetocaloric effect around room temperature are of increasing interest due to their possible application in magnetic cooling at room temperature. A significant boost to the field came about when it was realized that materials exist that provide giant entropy changes when driven in magnetic field due to the first order nature of the magnetic phase transition.^{1,2} Nevertheless the downside of first order behaviour is the large magnetic and thermal hysteresis (ΔH_M & ΔH_{th}), and associated loss in efficiency in the cooling cycle when the material is taken around a complete magnetic field or temperature hysteresis cycle. The itinerant metamagnetic $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ is one of the most interesting systems^{3,4,5} offering large ΔS of up to $120\text{kJm}^{-3}\text{K}^{-1}$ in a field change of 0-2T,³ coupled with an unusually low ΔH_M . It has also been shown that preparation of the material by the melt-spinning technique acts to reduce extrinsic contributions to ΔH_M and ΔH_{th} .⁴ Nevertheless understanding the contributions to the entropy change, ΔS , and associated hysteresis is one of the most challenging problems in this field today.⁶

A considerable effort has been dedicated to studying the entropy change in terms of lattice, electronic and magnetic contributions, although convergence of views is not yet complete. From a localized moment model,⁷ it has been suggested that in $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$, the lattice ΔS adds in opposition to the magnetic ΔS , in part because $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ belongs to the Invar family of materials that show a lattice contraction when heated. Theoretical work on the band structure of $\text{La}(\text{Fe},\text{Si})_{13}$ suggests that the low intrinsic hysteresis observed for this system is dependent on the presence of multiple shallow minima in the free energy⁸ as a function of the magnetic moment, thereby associating hysteresis with the energy barriers that separates the different magnetic phases of the material. Experimental work on hydrogenated samples under pressure⁹ offers strong support for this model. The significant volume of work from Fujita, Fukamichi and co-workers¹⁰ provides insight into the magnetic behaviour in terms of spin fluctuation theory and concludes

that the latent heat in the system is directly related to the change in magnetic state. Indeed the system shows a large change of magnetization.¹ Clearly a direct measure of the separate contributions to entropy change would further our understanding of this important system.

Here we study the calorimetric and magnetic behaviour of melt-spun $\text{LaFe}_{11.6}\text{Si}_{1.4}$, and by using two different calorimetric probes we separate latent heat and equilibrium heat capacity changes. A similar methodology has been set out by Marcos et al.^{11,12} We find that although the total ΔS in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ is comparable with other forms of the material such as arc melted bulk material,¹³ unlike this form and first order metamagnetic antiferromagnets such as CoMnSi ,¹⁴ it is the changes in the equilibrium heat capacity that provides the major contribution to the total ΔS in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ in its melt spun form.

2. Experimental

A $\text{LaFe}_{11.6}\text{Si}_{1.4}$ alloy was prepared by arc melting in Ar atmosphere and subsequent melt spinning. The surface speed of the rotating copper wheel was 30 m/s. The as-spun ribbons were annealed at 1050 °C for 2 h followed by quenching in water. According to Rietveld refinement of X-ray data the ribbons contained the La(Fe,Si)_{13} phase and a minor amount of $\alpha\text{-Fe}$ (about 5 wt.%). The Curie temperature of the prepared ribbons was estimated from the Arrott plots to be 185 K.

Magnetization and calorimetry measurements were carried out in fields up to 8T and temperatures ranging from 80-295K. Latent heat and ac calorimetry measurements were performed on approximately 100x50x30 μm sized fragments taken from a melt-spun ribbon.

The ac heat capacity measurement¹⁵ is operated in helium exchange gas, using an ac temperature ripple of (in this case) 0.07K at a frequency, $f=5\text{Hz}$, generated by resistive heater strips. The

change in sample temperature is measured using a phase sensitive lock in technique (at 2f, with a 1s time constant) to detect the voltage generated across the thermopile. Latent heat can only be captured if the ‘temperature ripple’ is large compared to the thermal hysteresis of the sample which is not the case here as the thermal hysteresis is approximately 0.8K at T_c . A thorough discourse on why latent heat cannot be fully captured using the ac calorimetric technique has also been discussed elsewhere.¹⁶ The latent heat probe,¹⁷ in contrast is set up in vacuum. We only use the probe at fixed bath temperature in swept magnetic field mode. There are two important time scales; the system relaxation time to the bath temperature which is of the order of 1s and the magnetic field sweep rate which is 8.3mT/s. This probe captures the latent heat component fully. Therefore we use the ac calorimetry probe to determine the equilibrium change in heat capacity at zero and fixed field and the latent heat probe to determine the latent heat component.

To calculate the entropy change of the fragment due to latent heat (ΔS_{LH}) or the change in heat capacity (ΔS_{HC}), equations (1) and (2) are used,

$$\Delta S_{LH} = -\Delta Q_L / T \quad (1)$$

$$\Delta S_{HC}(T > 185K) = \int_T^{T1} ((C(H, T) - C(0, T)) / T) dT \quad (2)$$

where ΔQ_L is the heat output due to latent heat at temperature T (calibrated using a reference pulse as described in ref 17), and $C(H, T)$ is the heat capacity in magnetic field H (chosen to be 4T) at T. The reference temperature, T1, used in the integral of Eq. (2) was chosen as 240K. A finite zero field latent heat term exists at T_c in this system, which means that when integrating from 240K to below T_c (=185K) this needs to be added to Eq. (2) to fully account for a change of state from PM to FM.

$$\Delta S_{HC}(T < 185K) = \int_T^{T1} ((C(H, T) - C(0, T)) / T) dT + \Delta S_{LH}(FM \rightarrow PM)|_{T_c} \quad (3)$$

Further details of the experimental techniques used are given elsewhere.^{14,15,17} The total, $\Delta S_{\text{total}} = \Delta S_{\text{HC}} + \Delta S_{\text{LH}}$, can be compared to the entropy calculated from bulk samples,^{14,18} which is calculated here by numerical integration of isothermal M-H loops using the Maxwell relation.⁶

It is known that in this system there is coincident isostructural volume expansion during the transition from the paramagnetic (PM) to the ferromagnetic (FM) state of the order of 1.5%.¹⁹ Here we use the heater resistance, R_h , embedded in the silicon nitride membrane, as a measure of the expansion in one dimension.¹⁵ The change of R_h due to lattice expansion of the sample is not calibrated precisely, but it provides a useful and reproducible guide to volume changes alongside heat capacity measurements. Similar results were obtained from several samples when normalized by mass.

3. Results and Discussion

Figure 1 shows the M - H loop of a melt-spun ribbon with dimensions of 2 mm x 1mm x 0.03mm and the magnetic field applied perpendicularly to the plane of the sample at a sweep rate of 0.5T/min. We also look at the properties of thirty $\sim 100\mu\text{m}^3$ sized melt-spun fragments taken from the sample to see how fragmentation affects the magnetization properties. The ΔH_M in the melt-spun samples is already small but the data shows that fragmentation reduces this even further. Although the onset field in bulk and fragment is similar, a larger applied field is required to complete the transition in the fragments. In this sense the transition is broadened in the fragment. Note that the saturation magnetization in the collection of fragments is slightly lower, and from figure 1(b) it can be seen that the phase line is suppressed by approximately 2K.

Figure 1 – a) M - H loop of whole (solid curve) and fragmented ribbons (dashed curve) when the field is aligned perpendicular to the sample plane at 192.5K, 195K, 197.5K and 200K. b) H - T phase diagram from this data (whole ribbon ■, fragments □), where H_c is determined as the point at which M is 50% of its saturation value. The phase line of the fragments cuts the x axis at 187.5K and that of the bulk at 189.5K, suggesting that fragmentation results in a lower T_c .

Figure 2 shows the heat capacity and latent heat measurements explicitly. It is important to note that the heat capacity peak feature shown in figure 2(a) is not associated with latent heat. It does not mirror the change of sign on reversing the magnetic field direction (indicated by solid and open symbols) that is seen for the latent heat spikes shown in figure 2(b), and the temperature evolution of the magnitude of the peak in heat capacity (which first increases as the temperature is increased away from T_c) and the latent heat spikes (which decrease rather linearly with increasing temperature away from T_c) are also quite different. The combination of these observations, as well as arguments given elsewhere,¹⁶ support the view that ac calorimetry does not capture latent heat. We therefore believe that the features captured with the ac heat capacity probe are related to spin fluctuations as discussed elsewhere¹³ and they are clearly enhanced and sharpened by the first order nature of the transition. Note that the data used to calculate ΔS_{HC} is taken from the curves at 0T and 4T as indicated in the schematic in the inset to figure 2(a).

Figure 2 - Raw data taken from micro-calorimetry. a) Change in heat capacity for increasing field (open symbols) and decreasing field (closed symbols), where for $T=188.5\text{K}$ to 193.5K , $C(0\text{T})$ varied from 0.49 to $0.45 \pm 0.05 \text{ kJ K}^{-1} \text{ kg}^{-1}$. The inset shows a schematic showing how ΔC ($0\text{T}-4\text{T}$) is extracted for use in Eq. (2). b) Latent heat for both field directions. c) Magnetostriction, $\Delta R/R$ [15] as a function of increasing field at temperature intervals of 2.5K . Note that as temperature increases the start and end fields in the volume expansion process diverge.

The magnetic field driven latent heat term shown in figure 2(b), is large and well-defined close to T_c and then drops rather linearly towards zero (in increasing temperature). Again this is entirely consistent with spin fluctuation theory, as discussed in more depth in Ref. [10]. (Note that because multiple peaks in latent heat are observed, the total ΔQ_L will be proportional to the integral of the signal shown in figure 2(b)). Above 201K the heat capacity shows large broad changes that are not mirrored in the latent heat but are reflected in the qualitative measure of magnetostriction, $\Delta R/R$, which is shown in figure 2(c). Interestingly $\Delta R/R$ changes from a sharp step like feature to a more continuous change as the temperature is increased away from T_c , which supports the suggestion that the move towards continuous behaviour observed here is due to thermal effects rather than a weakening of the spin-lattice coupling. As the temperature is increased the energy barrier between the equilibrium magnetic phases decreases, eventually tending to zero as the latent heat term tends to zero.

Figure 3 shows the contributions to ΔS determined calorimetrically, (from the two separate components measured in the heat capacity and latent heat probes), in two single fragments compared to ΔS obtained from the bulk (ribbon) magnetization measurements. The ΔS_{total} ($=\Delta S_{\text{HC}}+\Delta S_{\text{LH}}$) from two separate single fragments agrees well with $\Delta S_{\text{Maxwell}}$, and from this we can infer that the fragmentation process has not significantly changed the fundamental properties of the sample and also that our method of separating the contributions to the entropy change is robust i.e. the total calorimetric and the total magnetization contributions are comparable. The key observation is that in these melt spun materials the majority of $\Delta S(4T)$ comes from changes in the equilibrium heat capacity ΔS_{HC} at 0T and 4T, and that the ΔS_{HC} component is almost temperature independent. The magnitude of ΔS_{HC} drops to zero at a temperature where the critical field of the phase transition exceeds the maximum applied field which at 4T corresponds to $T>206\text{K}$ (see the phase line in figure 1(b)). Note that the bulk and fragment phase lines are shifted slightly. This shift is not manifest in figure 3 because the data points have been averaged over a 5K temperature span as part of the numerical integration process. It is interesting to note that the balance of these contributions to entropy change may be different in the arc melted material compared to other forms of this compound,¹³ suggesting that morphology and processing may affect the relative contributions of spin, electronic and lattice terms, even though the total entropy change remains equivalent.

The inset in figure 3 shows ΔH_{M} in the melt-spun sample as a function of temperature. The hysteresis is largest where the latent heat contribution is greatest, that is, close to T_{c} . As the temperature is increased ΔH_{M} decreases, tending towards zero where the latent heat term disappears. This observation supports the premise that at this temperature the energy barrier

between phases is overcome by thermal fluctuations¹⁰ and consequently the material shows no hysteresis. Above this temperature the transition is effectively second order

Figure 3 – Comparison of the ΔS contributions calculated from heat capacity ($\circ$) and latent heat (Δ) measurements of a ~ 100 micron melt-spun fragment. ΔS_{Total} ($\square$) is the sum of the two contributions and is comparable to $\Delta S_{\text{Maxwell}}$ for a $2 \times 1 \text{ mm}$ ribbon (solid line). Open and solid symbols indicate the results for two separate fragments, A and B respectively.

The adiabatic entropy change, ΔT_{ad} can be determined from heat capacity and magnetisation data by using equation (4).²⁰ Often however, if the field-dependent heat capacity at a given temperature is not known then ΔT_{ad} will be estimated by assuming that the heat capacity is independent of field as shown by equation (5). As stated elsewhere,²⁰ large changes in heat capacity in response to applied magnetic field will result in additional errors to the use of equation (5).

$$\Delta T_{\text{ad}}(T)_{\Delta H} = - \int_{H_i}^{H_f} \left(\frac{T}{C(T, H)} \right)_H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (4)$$

$$\Delta T_{\text{ad}} \approx \frac{T}{C(T)_H} \Delta S_M(T)_{\Delta H} \quad (5)$$

In the case of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound shown here, we have demonstrated explicitly that significant changes in heat capacity (of the order of 100%) occur about the phase transition. Fujita and Fukamichi¹³ infer by indirect measurement that there is an enhancement of heat capacity due to the amplitude of the thermal spin fluctuations in the paramagnetic phase. Their conclusions are supported by their observation of a factor of two enhancement of the paramagnetic susceptibility. The explicit field dependence of the heat capacity enhancement associated with spin fluctuations at a first order itinerant electron transition has not been previously reported (as far as we are aware), in part because of the difficulty of separating out the latent heat contribution. Here we have overcome that difficulty by measuring the heat capacity and latent heat contributions separately, and consistent with previous work,¹³ we can make an explicit association between the heat capacity peak feature and the significant spin fluctuations in these materials. The feature is clearly enhanced and sharpened by the first order nature of the transition. The impact of these large changes is to lower the maximum achievable ΔT_{ad} as was observed by a comparison of indirect and direct measurements of ΔT_{ad} by Fujieada *et al.*²¹ If the large enhancement of the heat capacity observed here is a general feature of itinerant electron metamagnetic systems, it is expected that ΔT_{ad} will always be limited in some degree by $C(H,T)$ whether the transition is of first or second order.

4. Conclusion

Our independent probes allow us to observe that in melt-spun $\text{LaFe}_{11.6}\text{Si}_{1.4}$ ribbons the change in the equilibrium heat capacity provides the dominant contribution to ΔS_{total} , even close to the zero field T_c of the system. We show that fragmentation of the sample lowers the effective hysteresis, which is an additional important observation for application of the material, although the process is neither controlled here nor fully understood and will be the subject of further study.

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Figure 1 (fig1.JPG)

Figure 2 (fig 2.JPG)

Figure 3 (fig 3.JPG)