Magnetocaloric effect of ferromagnetic CeAuGe

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Abstract. The magnetocaloric effect (MCE) may become strongly enhanced in systems exhibiting a second order magnetic phase transition due to critical behaviour of the order parameter in close proximity of the transition region. Recently it has been shown that, analogous to the order parameter, the MCE shows scaling behaviour with the applied magnetic field along the critical isotherm. It has been argued that this behaviour should be indicative of the universality class of the system. Using ferromagnetic CeAuGe as a model system with high crystallographic and atomic order, we have determined the MCE from specific heat measurements in various applied fields. In the low field limit we observe scaling behaviour reminiscent of a mean field ferromagnet. However, in progressively larger applied fields the MCE in CeAuGe significantly exceeds that of the mean field reference system, indicating that the refrigeration capacity of CeAuGe is significantly larger than that of a model mean field ferromagnet. Our results are contextualized in terms of a more general amenability of local-moment magnetic compositions as model systems for magnetic refrigeration.

1. Introduction

The magnetocaloric effect describes the reversible cooling or heating of a material under the action of a changing applied magnetic field. It is customary to express the magnetocaloric effect in terms of two parameters, each denoting a specific magnetic field induced trajectory in phase space. These are the isothermal entropy change $\Delta S(T)_{\Delta B}$ and the adiabatic (isentropic) temperature change $\Delta T_{\Delta B}(T_f)$. These parameters are defined in analogy with the well known Carnot gas-compression refrigeration cycle. Regarding the magnetocaloric effect this cycle consists of an initial isothermal magnetisation obtained by increasing the magnetic induction B from B_i to B_f which causes the entropy of the system to change by $\Delta S(T)_{\Delta B}$ (for the sake of simplicity we assume that the applied field H can be related to B through $B = \mu_0 H$). The second step is an isentropic demagnetisation (decreasing B from B_i to B_f) which induces an adiabatic temperature change $\Delta T_{\Delta B}(T_f)$ in the sample.

The simplest magnetic system exhibiting this effect is an ideal spin-1/2 paramagnet. In the limit where there are no interactions between the spins in the system and all entropy contributions other than the magnetic configurational entropy of the system are negligible, adiabatic demagnetisation cools the system down to absolute zero. In any real system however the former condition can never be met and it is found that magnetic interactions limit the lowest temperatures attainable via the MCE [1].

While interactions among magnetic moments generally act to the detriment of the MCE in paramagnetic systems they are responsible for a significant MCE in systems where such interactions are strong enough to cause a phase transition between the paramagnetic and a

magnetically ordered state. In systems where the transition is of second order the behaviour of a host of physical properties close to the phase transition temperature T_c is determined by the growth of a characteristic length scale over which coherent fluctuations in the order parameter occur [2]. In zero applied magnetic field this critical behaviour is manifested by the dependence of physical quantities on a reduced temperature ϵ. In the critical region the temperature dependence of physical quantities usually takes on a form dominated by terms of order ϵ^p. The value of p is characteristic of the universality class of the system.

For magnetic systems the magnetisation M is a natural choice for the order parameter. The critical behaviour of M with temperature in zero applied field as the critical phase transition temperature T_c is approached takes on the form

$$\left.\frac{\partial M}{\partial T}\right|_{B=0} \sim \pm\,|\epsilon|^{-\beta} \text{ for } \epsilon = \frac{T - T_c}{T_c} < 0. \tag{1}$$

The critical behaviour of M is suggestive of a significant magnetocaloric effect [3] as is discussed next. The isothermal entropy change in a system as it is magnetised by increasing B from B_i to B_f follows from the well-known Maxwell-relations as

$$\Delta S(T)_{\Delta B} = \frac{1}{\mu_0}\int_{B_i}^{B_f}\left(\frac{\partial M}{\partial T}\right)_B dB. \tag{2}$$

Due to the critical behaviour of M the integrand diverges as $T \to T_c$ and $B \to 0$ (see Eq.1). Therefore large $\Delta S_{\Delta B}$ values are expected in the vicinity of $T = T_c$ due to the critical contribution to the integrand. The critical behaviour of the MCE has been a topic of recent theoretical interest. It is known that the maximum value of $\Delta S(T)_{\Delta B}$ (hereafter referred to as ΔS_{max}) occurs at a temperature T' close to T_c if magnetisation proceeds from $B = 0$ to $B = B_f$ [3]. In the limit where $B_f \to 0$ the temperature T' approaches T_c. It could be shown by Franco et al. (see Ref. [4]) that $\Delta S_{max}(B_f)$ scales with the applied field as $|\Delta S_{max}(B_f)| \sim B_f^n$ and that n is indicative of the universality class of the system.

In this work we turn our attention to the MCE in CeAuGe. It has been noted that lanthanide systems are prime candidates for commercial applications of the MCE due to the large localised magnetic moments associated with the rare earth ions in these compounds. Within this context it may seem counter intuitive to study the MCE in cerium-based intermetallic compounds as the Ce^{3+} free-ion moment ($J = 5/2$) is relatively small when compared to other rare earth ions such as Gd^{3+} ($J = 7/2$). Furthermore in a host of crystalline systems (as is the case with CeAuGe, see Ref.[5]) the degenerate ground state multiplet associated with the free tri-positive Cerium ion is split by the action of an anisotropic crystalline electric field (CEF). In CeAuGe the CEF causes the magnetic ground state to be a doublet (corresponding to $J = 1/2$). The reason for studying the MCE in CeAuGe (and other Cerium systems) however can be seen when the mechanism by which magnetic order is established is investigated.

Magnetic order in lanthanide systems usually occurs due to an indirect exchange mechanism, whereby the magnetic moments localised at lanthanide crystallographic sites polarise the itinerant electrons in the system thereby producing an indirect interaction between neighbouring localised moments. Recent theoretical investigations into such systems has shown that the refrigeration capacity in these systems are enhanced due to the polarisation of conduction electrons [6, 7]. The local interaction between the $4f$-electron of the Ce^{3+}-ion and the conduction electrons in various Ce-based intermetallic systems is strong enough to produce an extensive range of correlated electron phenomena [8]. Given the possibility that such systems may show a significant enhancement in refrigeration capacity, the MCE in Ce-based systems is of conceivable interest. However, a systematic study into the magnetocaloric properties of Ce-based intermetallics is still generally lacking. Here we present a first investigation into the MCE

of CeAuGe, focussing on the critical behaviour of the MCE as well as the refrigeration capacity of the system.

2. Experimental Procedure

The synthesis and characterisation of polycrystalline CeAuGe is discussed in Refs.[5] and [9]. The MCE is calculated indirectly from the measured specific heat reported in the latter two references. The calculation follows the method given in Ref.[10]. The isofield entropy $S_B(T)$ is calculated from the specific heat $C_{p,B}(T)$ measured in constant pressure and applied field as

$$S_B(T) = \int_0^T \frac{C_{p,B}(T)}{T} dT. \tag{3}$$

Eq.3 introduces two significant errors into the results that follow. The first is the numerical error associated with calculating the integral from a discreet set of data points. The second is that the experimental temperature range does not extend down to absolute zero. This implies that the contribution from $\int_0^{T_0} \frac{C_{p,B}(T)}{T} dT$ (where T_0 is the lowest available experimental temperature) needs to be approximated through extrapolation. Both these errors are taken into account in the sections below.

Knowing $S_B(T)$ for a set of applied fields allows the isothermal entropy change $\Delta S_{\Delta B}(T)$ associated with $\Delta B = B_f - B_i$ to be calculated as

$$\Delta S_{\Delta B}(T) = S_{B_f}(T) - S_{B_i}(T) \tag{4}$$

In this work $B_i = 0$ is used throughout in the calculation of the $\Delta S_{\Delta B}(T)$ data reported in the next section. The adiabatic temperature change follows from

$$\Delta T_{\Delta B}(T_f) = T_f - T_i \tag{5}$$

where T_i and T_f have values satisfying the isentropic condition $S_{B_i}(T_i) = S_{B_f}(T_f)$. With regards to $\Delta T_{\Delta B}(T_f)$ it will be assumed that $B_f = 0$ throughout.

3. Results and Discussion

The various isofield entropy curves are calculated from the specific heat of CeAuGe as reported in Refs.[5] and [9]. Shown in figure 1 are the isofield entropy in zero applied field, 1 T and 9 T. The inset shows the magnetic configurational entropy calculated by considering the magnetic contribution to the specific heat. The latter is calculated by using the LaAuGe specific heat reported in [9] as a non-magnetic reference. The saturation value of the magnetic configurational entropy is close to $R \ln 2 = 5.76$ J.mol^{-1}.K^{-1}as is expected for a magnetic doublet. The calculation of the magnetic configurational entropy confirms the correct treatment of the errors inherent to Eq. 3 as noted in the previous section.

$\Delta S_{\Delta B}(T)$ and $\Delta T_{\Delta B}(T_f)$ calculated from $S_B(T)$ are shown in figures 2 and 3. Also shown is the magnetocaloric effect of an ideal $J = 1/2$ mean field ferromagnet with the same transition temperature as CeAuGe. In calculating the MCE of this model system the formalism developed in Ref.[11] was used. A comparison between the MCE in CeAuGe and the ideal mean field ferromagnetic system shows that the characteristic Caret-like shape (see for example Ref. [3]) of $\Delta S_{\Delta B}(T)$ and $\Delta T_{\Delta B}(T_f)$ is much broader for CeAuGe than for the mean field ferromagnetic system. As is discussed below this is an indication of the enhanced refrigeration capacity of CeAuGe. For $\Delta B = 1$ T the extremas in both $\Delta S_{\Delta B}(T)$ and $\Delta T_{\Delta B}(T_f)$ for CeAuGe are close to the corresponding extremas of the mean field system. This is the first indication that the critical behaviour of CeAuGe closely resembles that of a mean field ferromagnet in small applied fields.

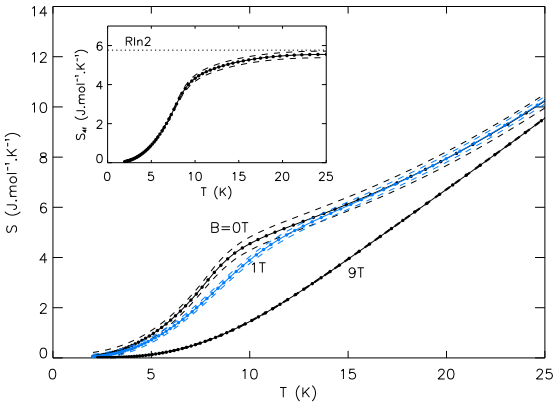

Figure 1. The isofield entropy (filled circles) for CeAuGe calculated from experimental specific heat data in zero field, 1 T and 9 T. Upper and lower bounds are indicated by dashed lines. Inset: Magnetic configurational entropy of the Ce^{3+} $4f$-electrons in CeAuGe in zero applied field.

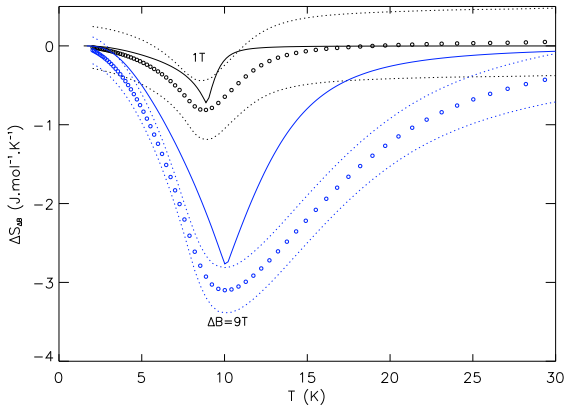

Figure 2. The isothermal entropy change $\Delta S(T)_{\Delta B}$ (open circles) calculated from the isofield entropy curves in figure 1 for $\Delta B = 1$ T and 9 T. Dotted lines show the uncertainty in the calculation. Solid lines show the isothermal entropy change calculated for the corresponding model mean field system.

In order to investigate the critical behaviour further $\Delta S_{max}(B_f)$ for both CeAuGe and the model mean field system are shown in figure 4. $\Delta S_{max}(B_f)$ for the mean field system lies within the margins of error (calculated for CeAuGe) up to $\Delta B = 4$T. For larger fields $\Delta S_{max}(B_f)$ in CeAuGe clearly exceeds that of the mean field system. The behaviour of $\Delta S_{max}(B_f)$ shown here suggests that the critical behaviour of polycrystalline CeAuGe closely resembles that of a mean field ferromagnetic system.

The refrigeration capacity of CeAuGe is calculated from figure 2 as

$$q(B_f) = \int_0^{\infty} \Delta S_{\Delta B}(T) dT \tag{6}$$

and shown in figure 4. The refrigeration capacity of the mean field system is also shown. We find that the refrigeration capacity of CeAuGe exceeds that of the mean field system by $\sim 40\%$ in all but the lowest applied fields.

4. Conclusion

The MCE in polycrystalline CeAuGe was calculated indirectly from measured specific heat data in various applied fields. It could be shown that the critical behaviour of the MCE in small applied fields is close to the critical behaviour expected in a mean field ferromagnetic system. Importantly, the refrigeration capacity of CeAuGe is shown to be significantly enhanced above that of the ideal mean field system, highlighting the role of local-moment magnetic compositions as model systems for magnetic refrigeration.

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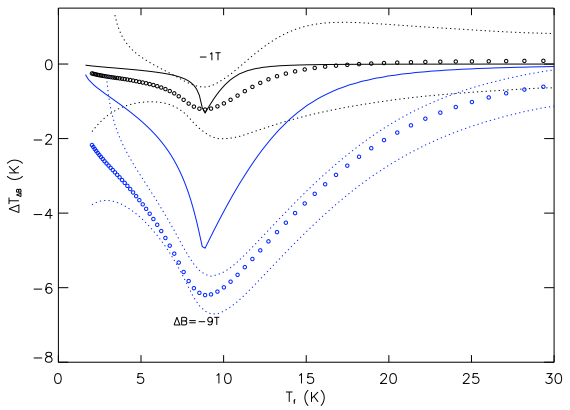

Figure 3. The adiabatic temperature change $\Delta T(T_f)_{\Delta B}$ calculated from the isofield entropy curves in figure 1 for $\Delta B = 1$ T and 9 T (open circles). Dotted lines show the uncertainty in the calculation. Solid lines show the adiabatic temperature change calculated for the corresponding mean field ferromagnetic system.

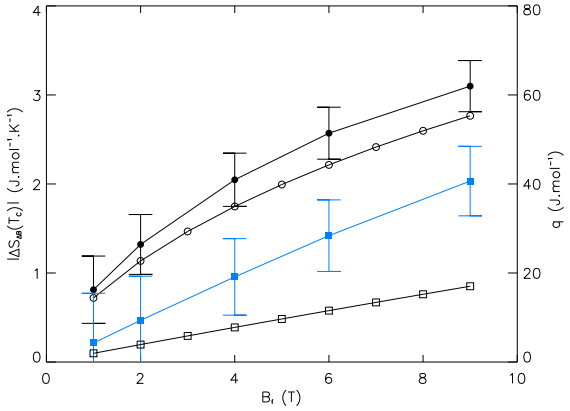

Figure 4. $|\Delta S_{max}(B_f)|$ for $\Delta B = B_f$ between 1 T and 9 T. Filled circles correspond to values calculated from the isofield heat capacities reported in Ref.[9] while the unfilled circles correspond to values calculated for the corresponding mean field ferromagnetic system. Note that the vertical axis on the left of the figure shows values for $|\Delta S_{max}(B_f)|$ in units of J.mol^{-1}.K^{-1}. The refrigeration capacity of CeAuGe (filled squares) is also shown, together with the refrigeration capacity of the mean field ferromagnet (unfilled squares). The vertical axis on the right of the figure shows values of the refrigeration capacity in units of J.mol^{-1}.

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