The determination of critical behaviour of ferromagnetic CeCuGe using magnetocaloric effect

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Abstract. Critical behaviour of magnetic systems associated with a second order phase transition is of general interest in condensed matter physics as a useful tool to study universal behaviour across a wide range of magnetic systems. Typically a specific universality class is characterized by a set of critical exponents which determine the type of divergences occurring in thermo-magnetic quantities as the phase transition temperature is approached. Here we present results obtained from specific heat and magnetization measurements of CeCuGe. Isothermal magnetization of hexagonal, highly crystallographic ordered CeCuGe was measured across the paramagnetic to ferromagnetic phase transition in order to study resulting critical phenomena. From the analyses of the magnetization data, T_{C} was confirmed using the Arrot-plot technique. The critical exponents, β, γ and δ obtained from fits of the spontaneous magnetization, magnetic susceptibility and isothermal magnetization revealed that the system behaves as a mean field ferromagnet. An independent analysis of the critical behaviour is presented in terms of the magnetocaloric effect (MCE) and shows good agreement with the results derived from Arrot-plots analysis.

1. Introduction

The magnetocaloric effect describes the *reversible* heating or cooling of a magnetic system by changing the applied magnetic field to which a sample is exposed [1]. The effect has its origin in the change of magnetic configurational entropy induced by a changing applied magnetic field which is compensated for (under isentropic conditions) by a corresponding change in entropy in the non-magnetic sub-system (typically the crystalline lattice). Over the last two decades increasing attention has been paid to the magnetocaloric effect (MCE) in a variety of magnetic compounds due to the discovery of the so called 'giant' magnetocaloric effect in $Gd_5Si_2Ge_2$ [2]. Much of these recent efforts have been directed at finding suitable materials for use as room temperature magnetic refrigerants as an energy efficient alternative to gas-compression refrigeration cycles. The increasing scientific importance attributed to the MCE as a result of these studies established several protocols by which the MCE may be used as a fundamental probe into the magnetic state of a particular material in addition to more 'traditional' characterisation methods such as magnetometry and calorimetry. One such protocol is the determination of the universality class of a material through its magnetocaloric effect [3].

The feasibility of this protocol has been well established in literature for a group of soft, amorphous ferromagnetic materials [4]. However, experimental investigations into the applicability of this method to a broader family of magnetic systems are still incomplete. One particular family of systems amenable to the study of this protocol is the class of Ce-based ferromagnetic systems in which strong hybridisation effects between the Ce^{3+} $4f$-electrons and the conduction band electrons are absent [5]. It is noted (on purely phenomenological grounds) in ref.[5] that this class of systems seem to establish ferromagnetic order preferentially through long range exchange interactions, implying that these compounds should belong to the same universality class containing model mean-field ferromagnets. Within this context the ternary intermetallic compound CeCuGe has been chosen for the current study, as is motivated next.

CeCuGe crystallizes in a hexagonal structure type belonging to the AlB_2 family [6]. The ordered ternary phase crystallizes in the ZrBeSi-type structure with space group $P6_3/mmc$ (number 194) and is characterised by a unit cell elongated in the direction of the c-axis (the latter almost double the length of the a-axis. The atomic arrangement of CeCuGe in the unit cell is described as Ce-ions arranged in flat planes perpendicular to c-axis which are well separated by Cu-Ge layers [6]. In this crystal structure the Ce-site has $\bar{3}$m point symmetry [7], which profoundly affects the ground state of the Ce^{3+} $4f$-electrons responsible for magnetic ordering through the crystalline electric field (CEF) interaction. An analysis of the specific heat of CeCuGe revealed the presence of a Schottky anomaly resulting from the upliftment of the 6-fold degenerate free $4f$-electron multiplet by the CEF into a level dispensation of lower degeneracy [8]. The Schottky contribution to the specific heat could be parameterized by an energy separation of $\Delta_1/k_\mathrm{B} = 140$ K and $\Delta_2/k_\mathrm{B} = 205$ K separating two excited doublets from a doublet $4f$-electron groundstate [9]. It has been established that a transition to a ferromagnetically ordered state in CeCuGe occurs at $T_\mathrm{C} = 10$ K [10]. This has been verified with independent measurements of the specific heat (C_p) [9] where a prominent λ-type anomaly is observed at the transition temperature. The field dependence of the latter is consistent with ferromagnetic order.

For ferromagnetic systems it is expected that the magnetisation $M(T)$ and susceptibility $\chi(T)$ obey scaling laws $M \sim t^\beta$ and $\chi(T) \sim t^{-\gamma}$ (where t denotes a reduced temperature scale) in the vicinity of $T = T_C$ and in zero applied field, with $\beta = 0.5$ and $\gamma = 1$ for mean field systems [11]. Empirically it is known that in the critical temperature region ferromagnetic systems obey the Arrot-Noakes equation of state [12]

$$H^{1/\gamma} = a(T - T_C)M^{1/\gamma} + bM^{1/\gamma+1/\beta} \tag{1}$$

which allows for the determination of β and γ from Arrot plots [12]. The critical exponents determined from this analysis for CeCuGe yielded $\beta = 0.637(1)$ K, $\gamma = 0.962(2)$ K and the calculated $\delta = 2.509(1)$ K [13], suggesting that CeCuGe belongs to a class of mean field ferromagnets. The mean-field nature of this system implies that CeCuGe is a prime candidate compound with which to study the applicability of the above mentioned MCE protocol [3] outside of the narrow family of amorphous ferromagnets hereto investigated in literature. For this protocol to apply, the critical exponent characterising the field dependence of the MCE must correspond to that expected for a mean field ferromagnetic system.

2. Experimental procedure and sample characterisation

A polycrystalline CeCuGe sample was prepared in an arc furnace under ultra-high purity argon atmosphere. Stoichiometric amounts of the elements (purities in wt. %) Ce (99.99), Cu (99.995) and Ge (99.9999) were used. The ingots were remelted several times to promote homogeneity.

Powder x-ray diffraction (XRD) recorded using Cu K_α radiation of wavelength $\lambda = 1.5406$Å confirmed the formation of single phase CeCuGe. The measured data were fitted against the theoretical parameters [14] of the ZrBeSi-type structure. A Rietveld refinement profile according to the ZrBeSi-type structure (space group $P6_3/mmc$, number 194) was performed with calculated lattice parameters $a = 4.2987(8)$ Å and $c = 7.952(2)$ Å showing good correspondence with values previously reported in literature [14, 15]. The refinable parameters were instrument offset, the data background, unit cell parameters as well as full width half maximum (FWHM) of the peaks.

A SQUID magnetometer (Magnetic Properties Measurement System, Quantum Design, San Diego) was used to obtain the magnetization data used for the Arrot-plot analysis. The heat capacity option of a Physical Properties Measurement System (Quantum Design, San Diego) was used to obtain the specific heat of CeCuGe, from which the MCE is subsequently determined.

3. Results and discussion

Critical exponents in the vicinity of the Curie temperature were determined by Arrot plots technique [12]. These results were presented in our earlier reports [13], and are briefly summarised below. Magnetization data was plotted in the form M^2 vs $\mu_0 H/M$. The spontaneous magnetization $M_\mathrm{s}(T,0)$ values were computed from y-intercept of this graph, and inverse initial susceptibility $\chi_0^{-1}(T)$ values were computed from the x-intercept. The values of these intercepts were determined for a number of magnetic isotherms around $T = T_\mathrm{C}$. The T dependence of the intercepts were then fitted according to the expressions [16]:

$$Y(T) = -M_s\left(\frac{\partial M_s}{\partial T}\right)^{-1} = -\frac{T - T_C}{\beta}, \tag{2}$$

$$X(T) = \chi_0^{-1}\left(\frac{\partial \chi}{\partial T}\right)^{-1} = \frac{T - T_C}{\gamma}, \tag{3}$$

where β and γ are fitting parameters and T_C is determined by the requirement that the associated isotherm is linear in $\mu_0 H/M$ and passes through the origin. The range of the applied magnetic field used in this analysis is 0 to 2 T, and the results are shown in figure 1.

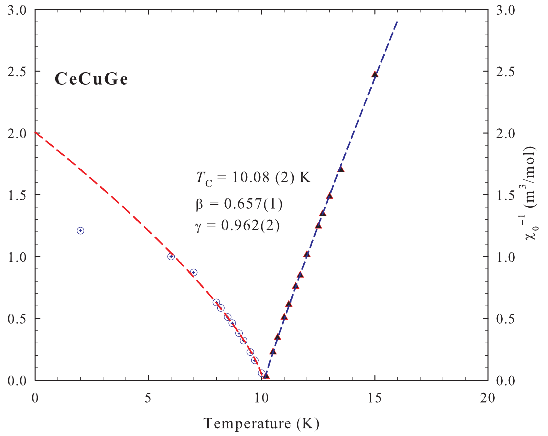

Figure 1. Spontaneous magnetization vs temperature (left hand axis),and initial susceptibility vs temperature (right hand axis).

The magnetocaloric effect is typically described in terms of two functions. The first is the change in entropy $\Delta S_{\Delta H}(T)$ resulting from an isothermal magnetisation process, increasing the applied field from an initial value H_i by an amount ΔH. For the values of $\Delta S_{\Delta H}(T)$ shown below an initial field of zero has been used throughout, implying that $\Delta H = H_f$. The second function describing the MCE is the change in temperature $\Delta T_{\Delta H}(T_i)$ resulting from a demagnetisation process achieved by decreasing the applied magnetic field while the sample is completely isolated from its surroundings. Here T_i denotes the temperature of the sample before demagnetisation. For the values of $\Delta T_{\Delta H}(T_i)$ shown below the final value of the applied magnetic field is zero throughout. As discussed above, $\Delta T_{\Delta H}(T_i) = T_i - T_f$ where T_i and T_f are determined by the isentropic condition $S(H_f, T_f) = S(H_i, T_i)$. Both $\Delta S_{\Delta H}(T)$ and $\Delta T_{\Delta H}(T_i)$ calculated for

CeCuGe are shown in figure 2. In order to contextualise these results, $\Delta T_{\Delta H}(T_i)$ calculated for a spin-1/2 mean field ferromagnet is shown in figure 3. From the figure it can be seen that the points where $\Delta T_{\Delta H}(T_i)$ is maximum traces out a straight line $T_i = T - T_C$ for the model system. This behaviour is putatively ascribed to the limitation placed on short range magnetic correlations inherent to the mean field model: in the classic mean field limit (see for example ref.[11]) the critical region is assumed to be infinitely small in temperetare and no short range correlations exist immediately above $T = T_C$. Similar behaviour is also observed for $\Delta T_{\Delta H}(T_i)$ calculated for CeCuGe, consistent with CeCuGe being a mean field ferromagnet.

According to the protocol established in ref.[3], the maximum values of $|\Delta S_{\Delta H}(T)|$ are expected to show scaling behaviour with the applied field so that:

$$|\Delta S_{\Delta H}(T)| \sim H_f^n, \tag{4}$$

n is derivable from the critical exponents β, γ and δ (see again ref.[3]) and is expected to have a value $n = 2/3$ for mean field systems. The scaling behaviour of $|\Delta S_{\Delta H}(T)|$ is also shown in figure 3. To a good approximation, the expected scaling law is satisfied up to $H_f = 90$ kOe and the value of $n = 0.62$ is derived by fitting the data in figure 3 by fitting the data to the behaviour expected from equation (5).

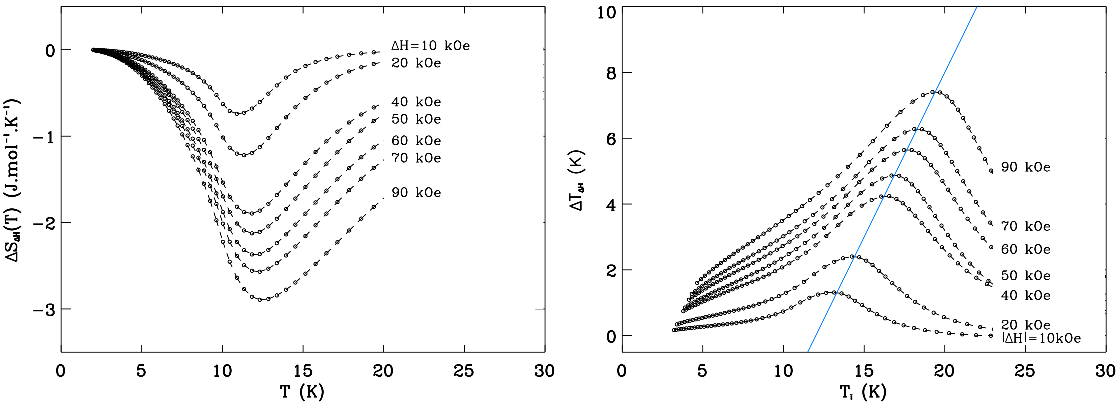

Figure 2. The isothermal change in entropy $\Delta S_{\Delta H}(T)$ (left) and the adiabatic change in temperature $\Delta T_{\Delta H}(T_i)$ (right) for CeCuGe as calculated from the specific heat data reported in [17]. The straight line in the right panel shows the locus $T_i = T - T_C^*$.

4. Conclusion

The protocol established by Franco *et al.* [3] by which the universality class of a system may be determined from an analysis of the magnetocaloric effect promises a powerful, yet simple technique by which critical behaviour in a magnetically ordered system may be characterised. This has been done with great success for a family of amorphous soft ferromagnets [18]. Here this protocol is applied to a completely different system, CeCuGe, forming part of a larger group of Ce-based ferromagnets [13]. Within the latter group mean field ferromagnetism is expected to predominate [5], and from an analysis of magnetisation data it could indeed be shown that CeCuGe is a mean field ferromagnet. Our analysis of the MCE in CeCuGe shows that both the peak values of the adiabatic temperature change $\Delta T_{\Delta H}(T_i)$ and the isothermal change in entropy $|\Delta S_{\Delta H}(T)|$ follow trends expected for, firstly a mean field ferromagnet, and secondly from the more general theory developed by Franco *et al* [3]. Specifically, the value of n, characterising the field dependence of the maximum values of $|\Delta S_{\Delta H}(T)|$ is found to be 0.62, close to $n = 2/3$

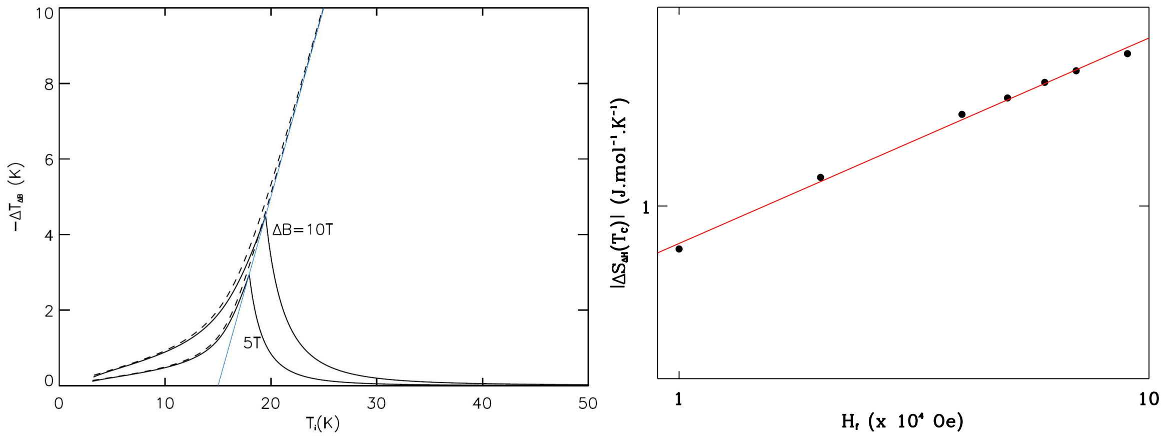

Figure 3. Left: $\Delta T_{\Delta H}(T_i)$ calculated for a spin-1/2 mean field ferromagnet. Dashed lines show asymptotic behaviour in the limit where the lattice contribution to the system entropy is negligible. The solid blue line is described by $T_i = T - T_C$. Right: The behaviour of $|\Delta S_{\Delta H}(T)|$ with applied magnetic field. The solid line shows the best fit of the scaling relationship $|\Delta S_{\Delta H}(T)| \sim H_f^n$ with $n = 0.62$.

expected for a mean field ferromagnet. In this analysis we implicitly assume that the exchange interaction responsible for ferromagnetism in CeCuGe is isotropic, and that in the vicinity of the Curie temperature anisotropy effects play a role secondary to critical fluctuations. This assumption is at least partially justified by the absence of strong anisotropy effects in the MCE (as was observed in polycrystalline $PrNiGe_2$ [19]) and by the fact that, although anisotropy effects result in different signatures in the MCE and magnetisation data, the critical exponents derived from both methods show close agreement. It is however hoped that a future study of a single crystal sample of CeCuGe will illuminate the validity of this assumption.

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