The magnetocaloric effect in ferromagnetic PrSi: evidence of a novel magnetic ground state and higher order exchange interactions

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Abstract. The discovery by Pecharsky et al. of the giant magnetocaloric effect (MCE) in $Gd_4Si_2Ge_2$, a member of the substitution series $GdSi_{4-x}Ge_x$ has generated significant interest into MCE phenomena in rare earth intermetalic compounds. Much recent effort has gone into determining how the MCE in such systems is influenced by the many salient features associated with rare earth magnetism. Here the MCE in polycrystalline ferromagnetic PrSi is determined from specific heat measurements. While the magnitude of the MCE in PrSi is found to be modest when compared to other binary systems, the power of MCE analyses in probing electronic and ground-state properties in magnetic systems is emphasized in this work. We forward a description in terms of a novel magnetic ground state for the $4f$-electrons associated with the Pr^{3+}-ions in this particular compound. It is found that the MCE in this system can be accurately reproduced by modelling the system as a modified Ising-type ferromagnet with the addition of a significant higher order exchange term and assuming that the ground state of the $4f$-electrons is the unperturbed 9-fold degenerate free-ion spin-orbit coupled ground state multiplet. Such a ground state would imply that the usual splitting of the degenerate energy levels of the free ion multiplet by the crystalline electric field is absent in this system, which in turn implies that significant multipolar interactions may be responsible for the higher order exchange terms present in the magnetic Hamiltonian.

1. Introduction

The magnetocaloric effect (MCE) was first defined as a reversible temperature change induced in a material through the action of a varying magnetic field [1]. However it has now become standard practice to define the MCE in terms of two parameters describing specific trajectories within the system phase space [2]. The first is an isothermal change in entropy $\Delta S(T)_{\Delta H}$ induced in the system by magnetising the sample while maintaining good contact with a heat bath at temperature T. The second parameter is an adiabatic change in temperature $\Delta T(T_i)_{\Delta H}$ obtained by isolating the sample from its surroundings at temperature T_i and demagnetising the sample isentropically. For convenience it is assumed throughout this work that the applied magnetic field H may be related to the magnetic induction through $B = \mu_0 H$.

Recent research regarding the MCE in rare earth intermetallic compounds may be classified in terms of two distinct objectives. The first is finding magnetocaloric materials which may be utilized for commercial applications (see for example the review by Tishin, Ref.[3]) while the second objective has been to gain a better understanding of how the MCE is influenced by some

of the features unique to rare earth magnetic systems [4]. It is within the latter context that this work is presented.

PrSi is known to order ferromagnetically at $T_C \simeq 54$ K [5, 6]. However, the magnetic ground state of this compound has not yet been characterised in detail. The compound crystallizes in the orthorhombic FeB-structure (space group *Pnma*), as do the other members of the RSi (R = La-Sm, Gd-Tb) family of compounds. Within this family PrSi and NdSi are the only two members to exhibit ferromagnetic order [5]. Similar behaviour in the RB_4 series of compounds has been attributed to significant orbital angular momentum contributions to the magnetic moments localised at rare earth crystallographic sites [7]. However, from symmetry considerations alone, it is expected that the 9-fold degenerate $J = 4$ spin-orbit coupled ground state multiplet associated with the $4f$-electrons of the free Pr^{3+}-ion should be split into nine non-degenerate (and typically non-magnetic) singlet states through the action of the crystalline electric field (CEF) [8]. In such systems the emergence of cooperative magnetic behaviour requires a secondary interaction mechanism. One such example is the establishment of ferromagnetic order through the formation of a pseudo doublet, produced through the admixture of the two lowest lying singlet states. Such a mechanism has been shown to produce magnetic order in TmNi (see Ref.[8]), which also crystallises in the orthorhombic FeB-structure.

In this work we show that the specific heat of PrSi is suggestive of the full nine fold degenerate $J = 4$ multiplet being the correct $4f$-electron ground state in this system, contrary to the point charge model calculations reported in Ref.[8]. While the magnetic configurational entropy is amenable to our proposed ground state, the strongest evidence supporting our claim is found by analysing the MCE in the system in conjunction with a simple numerical model.

2. Experimental Procedure

Two PrSi samples and one sample of the non-magnetic reference compound LaSi were prepared by melting together stochiometric amounts of the constituent elements in an arc-furnace under argon atmosphere. The first PrSi sample (hereafter referred to as sample A) was prepared from 99.99 wt.% purity Pr and 99.9999 wt.% Si. The second sample (hereafter sample B) was prepared from 99.9 wt.% purity Pr and 99.9999 wt.% Si. The LaSi sample was prepared from of 99.9 wt.% La and 99.9999 wt.% purity Si. During the melt samples were flipped and remelted several times to ensure homogeneity.

Powder X-ray diffraction was used to determine the phases present in all samples. X-ray diffraction was carried out on a Philips Panalytical X'pert Pro Instrument at room temperature using Cu radiation ($\lambda = 1.542$ Å) for the incident beam. The initial characterisation revealed that sample A had formed in the desired structure, whilst sample B and the LaSi sample both had small amounts of an impurity phase present in their respective diffractograms. Subsequently both sample B and the LaSi sample were annealed at 1000^0 C for 10 days. In preparation for annealing, samples were wrapped in tantalum foil and sealed in evacuated quartz tubes. X-ray diffraction showed the annealed samples to be predominantly single phase, with trace amounts of an unidentified impurity phase present in the diffractograms of both samples.

The specific heat results are derived from heat capacity measurements executed using the heat capacity measurement option of a Physical Properties Measurement System [9].

The numerical results are calculated from a model magnetic Hamiltonian using a simple Metropolis algorithm [10] on a $10 \times 10 \times 10$-element cubic lattice.

3. Results and Discussion

Figure 1 shows the X-ray diffractogram obtained for the as-cast sample of PrSi (sample A) together with a simulated diffractogram obtained for the orthorhombic *Pnma* FeB-type structure. The simulated diffractogram was obtained by using the lattice parameters and unit cell data reported for the FeB-structure type in [5, 11] as input to a full profile Rietfeld refining

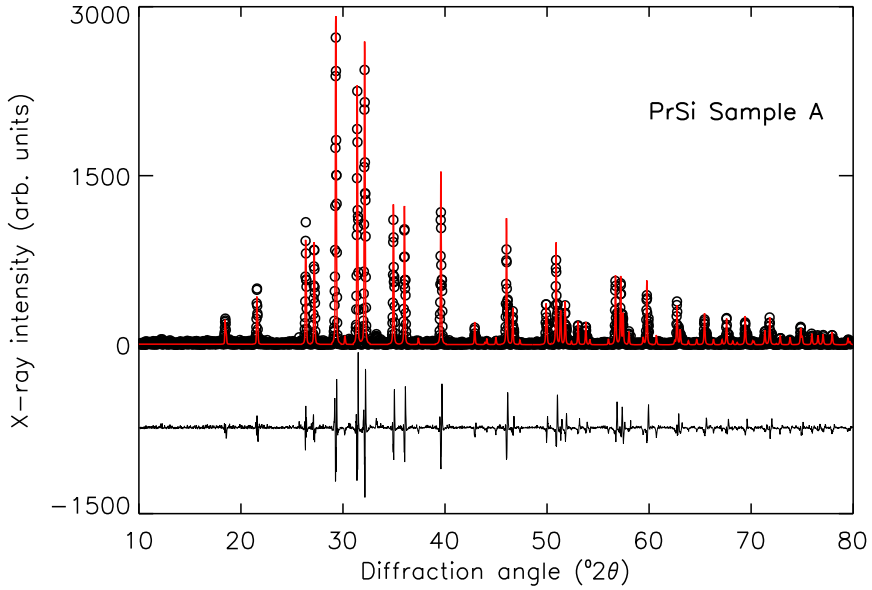

Figure 1. Powder X-ray diffraction spectrum (open circles) for PrSi sample A together with the spectrum calculated from a full profile least squares Rietveld refinement fit (solid line). The difference between the observed and simulated data is shown underneath the diffractogram.

program (GSAS, [12, 13]). The lattice parameters used to calculate the refined diffractogram are $a = 8.24362$ Å, $b = 3.94167$ Åand $c = 5.92000$ Å. A comparison between the simulated and measured diffractograms shown in figure 1 allows us to conclude that the sample formed in the desired structure. With the exception of a minor unknown impurity phase, similar results were obtained for sample B as well as the LaSi sample. As is shown below, the pressence of the latter impurity phase has a negligible effect on the specific heat of sample B.

The specific heat ($C_{p,\mathrm{PrSi}}$ and $C_{p,B=4T}$) of PrSi in applied fields of 0 T and 4 T together with the specific heat of LaSi ($C_{p,\mathrm{LaSi}}$) are shown in figure 2. The magnetic phase transition reported earlier [5, 6] is visible in the PrSi zero field specific heat as the prominent peak at $T_C = 51.74$ K. The inherent ferromagnetic nature of this transition is evidenced by the behaviour of the specific heat in an applied field of 4 T. The magnetic field acts to suppress and broaden the peak while simultaneously shifting the apex towards higher temperatures.

An attempt was made to calculate the contribution to the specific heat from the $4f$-electron magnetic configuration and thermal population of CEF-split levels ($C_{p,4f}$). The LaSi specific heat ($C_{p,\mathrm{LaSi}}$) was subtracted from the zero field specific heat of PrSi so that $C_{p,4f}(T) \simeq C_{p,\mathrm{PrSi}}(T) - C_{p,\mathrm{LaSi}}(T)$. A small Sommerfeld contribution ($C_s = \gamma T$ with $\gamma = 4 \pm 3$ mJ.mol^{-1}.K^{-2}) could be identified and subtracted from $C_{p,4f}(T)$. As shown in figure 3 $C_{p,4f}(T)$ does not show the typical Schottky contribution [14] associated with the thermal population of higher lying CEF-split energy levels, implying that such a splitting is completely absent from the system or that the experimental temperature range ($T \leq 300$ K) is less than a putative first thermal CEF excitation in PrSi. In order to test the first possibility it was assumed that $C_{p,4f}(T)$ is a purely magnetic configurational contribution to $C_{p,\mathrm{PrSi}}$, allowing the calculation of the zero field magnetic configurational entropy $S_{4f}(T)$ from the general equation

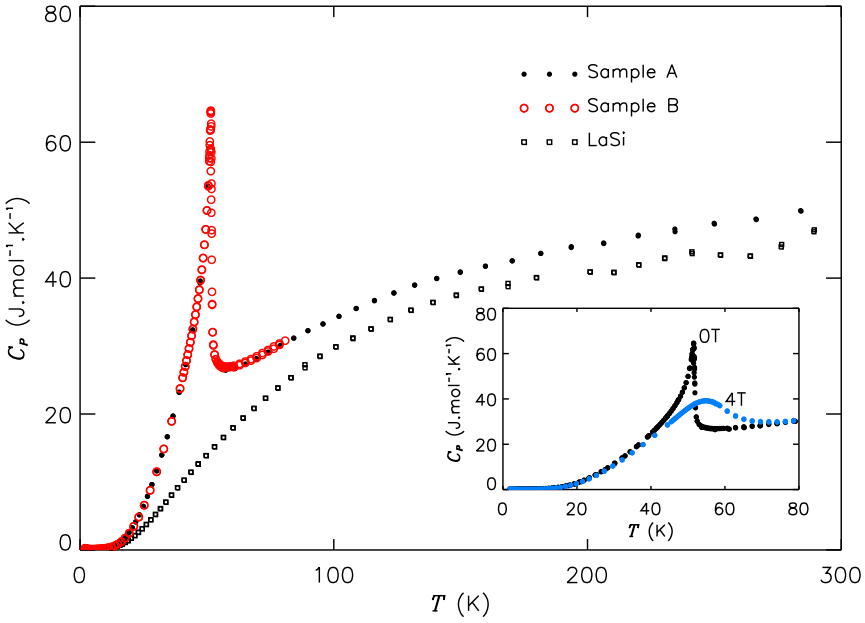

Figure 2. Specific heat C_p of PrSi and LaSi in zero applied field. Inset: PrSi specific heat in 0 and 4 T.

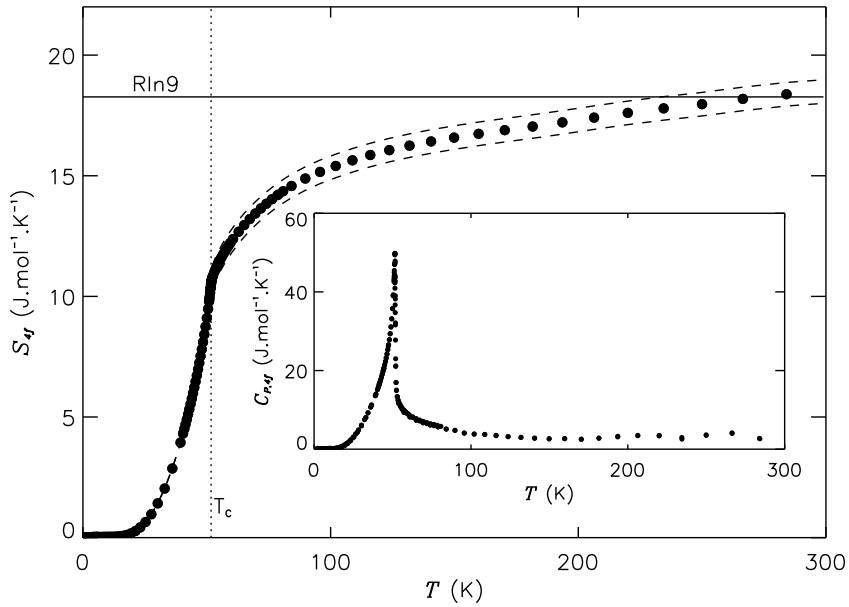

Figure 3. The $4f$-electron magnetic configurational entropy in PrSi. Inset: The $4f$-electron magnetic configurational specific heat contribution.

$$S_H(T') = \int_0^{T'} \frac{C_{p,H}(T)}{T} dT \tag{1}$$

The results are shown in figure 3. For a system containing magnetic moments where each

moment has N possible orientations the saturation magnetic configurational entropy is equal to $R \ln N$. Saturation occurs at a temperature where the population of all possible orientations become statistically equally probable. In PrSi the magnetic configuration entropy at T_C is already well in excess of $R \ln 2 = 5.76$ J.mol^{-1}.K^{-1}, ruling out the possibility of a pseudo doublet ground state. While the saturation magnetic configurational entropy associated with the $J = 4$ spin-orbit coupled free-ion ground state multiplet is approached at high temperatures, figure 3 shows that the entropy does not saturate within the experimental temperature region. This implies that the description of the non-magnetic specific heat contribution adopted earlier may not be adequate, or that there are non-negligible magnetic interactions present above $T = T_C$ that inhibit saturation. A third reason might be optical lattice excitations present in LaSi. This would imply that $C_{p,4f}(T)$ is underestimated in our calculation.

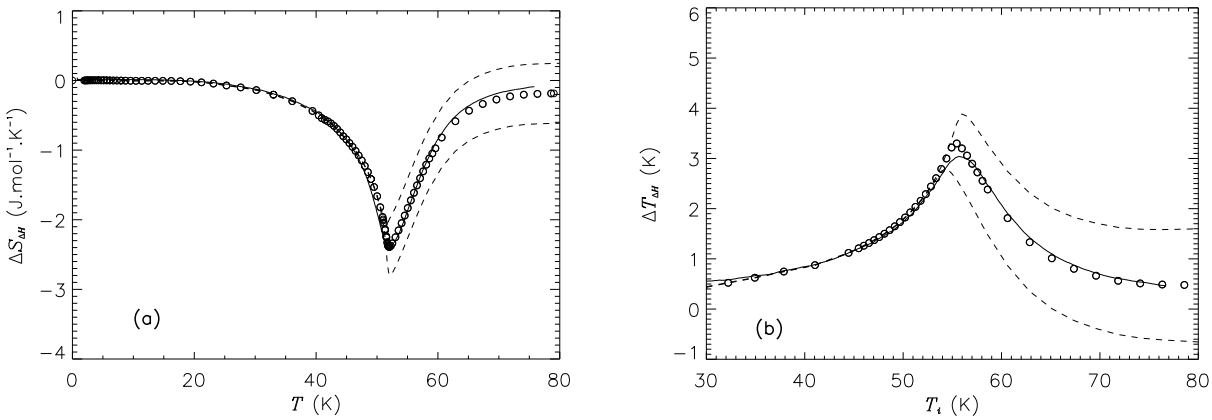

Figure 4. Isothermal entropy change upon magnetisation from 0 to 4 T (a) and adiabatic temperature change upon demagnetisation from 4 to 0 T (b). Uncertainties due to experimental errors are shown as dashed lines. Modelled results are shown by the solid lines.

In order to confirm the ground state of the $4f$-electrons in the system the MCE is calculated from the specific heat data (according to the method given in Ref.[15]) and analysed as is discussed below. Eq. 1 is used to calculate the isofield entropy from the specific heat data shown in figure 2 from which $\Delta S_{\Delta H}(T)$ and $\Delta T_{\Delta H}(T_i)$ are then calculated. The MCE thus calculated is shown in figure 4.

The shape of the MCE in the vicinity of a magnetic phase transition depends on the order of the transition [2], the behaviour of the correlation length associated with emerging magnetic order [16] as well as other site specific magnetic interactions such as those between localised moments and the CEF[4]. Through the Zeeman interaction the magnitude of the MCE depends strongly on the quantity $g \sum_i J_{z,i}$, where g is the Landé g-factor and $J_{z,i}$ is the component of the total angular momentum parallel to the quantization axis at site i.

Taking the above into account, an attempt was made to model the MCE in PrSi. Initial attempts to model the MCE in PrSi within the mean field [4] and pure Ising-model frame work assuming a pseudo doublet ground state failed to reproduce the experimental results accurately. The absence of CEF-effects in the $4f$-electron specific heat ruled out the addition of CEF-terms to the magnetic Hamiltonian. Instead, with reference to the RB$_4$ series of compounds noted earlier, we added higher order exchange terms to the magnetic Hamiltonian, in an attempt to better reproduce the MCE in PrSi. The best results where obtained by calculating the MCE in PrSi from a modified Ising model Hamiltonian containing higher order exchange terms, so that

$$\mathcal{H} = g\mu_B B \sum_i J_{z,i} + \mathcal{J} \sum_i \sum_j J_{z,i} J_{z,j} + \zeta \sum_i \sum_j J_{z_i}^2 J_{z,j}^2 \qquad (2)$$

The first term in the Hamiltonian denotes the Zeeman interaction while the second term is the traditional Ising-model exchange interaction between nearest neighbour sites. The third term is a higher order exchange term, also limited to nearest neighbour sites, and may originate from magnetoelastic exchange [4] or multipolar [17] interactions. It is found that for $g = 0.45$, $\mathcal{J} = 0.076$ meV and $\zeta = 0.011$ meV the magnetocaloric effect in PrSi can be reproduced accurately by assuming the ground state of the system incorporates the full $J = 4$ multiplet, as shown in figure 4.

4. Conclusion

The $4f$-electron contribution to the specific heat of PrSi suggests the likelihood of a spin-orbit coupled free-ion $J = 4$ multiplet ground state in PrSi. A pseudo-doublet ground state can be ruled out on account of the value of the magnetic configurational entropy at the phase transition temperature. The MCE in this compound can be accurately reproduced if a $J = 4$ multiplet ground state is assumed, CEF-effects are neglected and higher order exchange terms are added to the magnetic Hamiltonian. These latter terms are necessitated by the large orbital contribution to the magnetic moment implied by a $J = 4$ ground state, and consistent with the ferromagnetic order exhibited by PrSi in a family of otherwise predominantly antiferromagnetic compounds, analogous to the $R\mathrm{B}_4$ series. Detailed analyses on a single-crystal specimen that would allow the incorporation of magnetocrystalline anisotropy effects into our analyses are in progress.

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