The magnetocaloric effect in $PrNiSi_2$

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Abstract. The magnetocaloric effect (MCE) in lanthanide based compounds has attracted sustained interest ever since the discovery of the so called 'giant' MCE in $Gd_5Si_2Ge_2$. Apart from its applicability in new energy efficient refrigeration technologies, the MCE is also a very useful probe into the magnetic properties of a system. Recent research focuses on the interplay between the MCE and the salient features associated with 4f-electron magnetism. In this regard $PrNiSi_2$ is an interesting compound to investigate. The system is known to order ferromagnetically below 20 K contrary to the non-magnetic ground state expected for Pr^{3+} -ions in a crystalline electric field with orthorhombic symmetry. Subsequently a study of the MCE in polycrystalline $PrNiSi_2$ is presented. An anomalous contribution to the MCE is found above the magnetic phase transition temperature. An explanation of the latter in terms of a strong uniaxial anisotropy resulting from the leading terms in the CEF Hamiltonian is forwarded.

1. Introduction

The high temperature magnetic properties of systems containing rare earth ions can often be explained in terms of the magnetic properties of the free tri-positive lanthanides unmodified by a crystalline environment. This follows from the electron configuration of the lanthanides, where the partially filled $4f$-shell is shielded from the surrounding crystalline environment by the $5s$ and $5p$ orbitals [1]. The free-ion $4f$-electron ground state is determined by the spin-orbit interaction which produces a degenerate multiplet ground state characterised by the total angular momentum $\mathbf{J}$. For free Pr^{3+}-ions, the ground state multiplet is nine-fold degenerate ($J = 4$) and separated from the first exited multiplet by an energy (in temperature units) of $\Delta/k = 3100\,\mathrm{K}$ [1].

The shielding of the $4f$-electrons implies that the effect of the crystalline environment on the $4f$-electron states may be treated as a perturbation of the free-ion $4f$-electron Hamiltonian. The perturbation arises due to the Coulomb interaction between the $4f$-electrons and the charge clouds surrounding the crystallographic positions around the lanthanide ion crystallographic site. This crystalline electric field (CEF) adds terms of the form

$$\mathcal{H}_{CEF} = \sum_i \sum_n \sum_m B_n^m O_n^m(\mathbf{J_i}) \tag{1}$$

to the free-ion Hamiltonian. The $O_n^m(\mathbf{J_i})$-terms are so called *operator equivalents* and are listed in literature [2]. The *operator equivalents* are linear combinations of the operators

$$\mathbf{A_n} = \mathbf{J_z^n} \text{ where } n = 2, 4 \text{ or } 6 \tag{2}$$

$$\mathbf{B_m} = \mathbf{J_+^m} + \mathbf{J_-^m} \text{ where } m = 2, 4 \text{ or } 6 \tag{3}$$

$$\mathbf{A_n B_m} = \mathbf{J_z^n}(\mathbf{J_+^m} + \mathbf{J_-^m}) \text{ where } n + m = 2, 4 \text{ or } 6 \tag{4}$$

and

$$\mathbf{B_m A_n} = (\mathbf{J_+^m} + \mathbf{J_-^m})\mathbf{J_z^n} \text{ where } n + m = 2, 4 \text{ or } 6 \tag{5}$$

where $\mathbf{J}_+$ and $\mathbf{J}_-$ are angular momentum raising and lowering operators.

The terms in Eq.1 depends on the point symmetry of the crystallographic position of the lanthanide ion. $PrNiSi_2$ crystallises in a $CeNiSi_2$-type structure (space group $Cmcm$) [3] and is known to order ferromagnetically below $T_C = 20\,\mathrm{K}$ [4, 5]. In this structure the CEF-Hamiltonian associated with the Pr^{3+}-ion point symmetry becomes [6]

$$\mathcal{H} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6. \tag{6}$$

The effect of this Hamiltonian on the free-ion $4f$-electron multiplet may be gauged from Eqs. 2-5 as follows: operators with a zero superscript will add terms onto the main diagonal of the free-ion $4f$-electron Hamiltonian, uplifting the multiplet degeneracy but allowing for the system states to be described in terms of free-ion eigenstates. Operators with a non-zero superscript add off-diagonal terms to the free-ion Hamiltonian, implying that the new perturbed CEF-eigenstates are linear combinations of the unperturbed free-ion eigenstates. For Pr^{3+} it can be shown that this orthorhombic CEF Hamiltonian produces new eigenstates which are linear combinations of $|J_z\rangle$ and $|-J_z\rangle$ [7]. Such states have a zero magnetic moment which would therefore preclude the emergence of long range magnetic order.

Here we present a study of the magnetic state of $PrNiSi_2$ using the magnetocaloric effect (MCE) as a probe. The MCE describes the magnetic field driven reversible heating or cooling of a system [8]. Closely associated with this phenomena is the *isothermal* MCE, described as the isothermal change in entropy in a system resulting from a change in the applied magnetic field. The isothermal MCE in $PrNiSi_2$ provides strong evidence that O_2^0-terms in the magnetic Hamiltonian are the dominant CEF contributions, which in turn explains the emergence of magnetic order in this system, as is explained below. The pressence of O_2^0-dominated terms are also consistent with the uniaxial magnetic anisotropy of $PrNiSi_2$, reported in an earlier study [4].

2. Experimental procedure

A polycrystalline sample of $PrNiSi_2$ was prepared by melting together stoichiometric amounts of the constituent elements in an arc furnace under a purified argon atmosphere. The sample was prepared from 99.9 wt.% purity Pr, 99.99 wt.% Ni and 99.9999 wt.% Si. During the melt the button was flipped over and remelted several times to ensure homogeneity. The sample was subsequently wrapped in Ta-foil, sealed in an evacuated quartz ampoule and annealed at 1173 K for a month.

Powder X-ray diffraction was carried out on a Philips Panalytical X'Pert Pro instrument at room temperature. The sample stage is equipped with a sample spinner rotating the sample around the scattering vector to negate possible effects of preferred orientation in the powder. Cu radiation (Kα, $\lambda = 1.542\,\text{Å}$) was used for the incident beam.

The specific heat of $PrNiSi_2$ was measured by utilizing the Heat Capacity option on a Physical Properties Measurement System [9].

3. Results and discussion

Figure 1 shows the X-ray diffractogram obtained for $PrNiSi_2$ together with a spectrum simulated using Powdercell [10]. The simulation uses the lattice parameters and unit cell data reported in Ref.[5] for the *Cmcm* structure. A comparison between the intensity peaks in the diffractogram and those in the simulation shows that the sample predominantly formed in the desired structure.

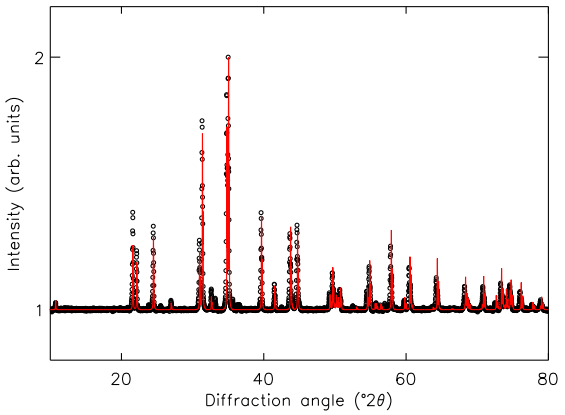

Figure 1. The powder X-ray diffraction spectrum for $PrNiSi_2$ (open circles) together with the simulated spectrum (red line).

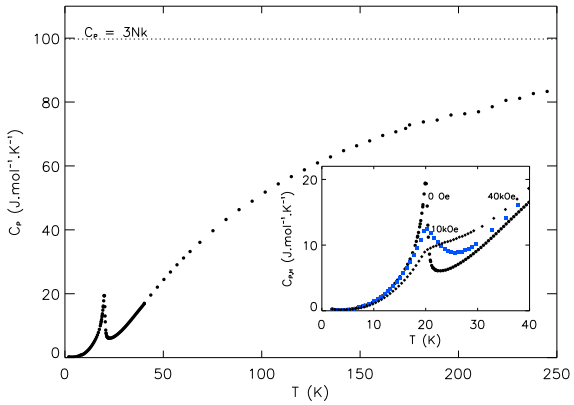

Figure 2. The specific heat of $PrNiSi_2$. The dotted line indicates the classical Dulong-Petit limit. Inset: The isofield specific heat of $PrNiSi_2$.

The specific heat of $PrNiSi_2$ is shown in figure 2. The onset of magnetic order is evidenced by the discontinuity appearing at $\sim 20\,\mathrm{K}$, consistent with earlier studies cited in the introduction. The field dependence of the low temperature specific heat is consistent with ferromagnetic order as the application of a magnetic field broadens the transition, while simultaneously suppressing and shifting the apex towards higher temperatures.

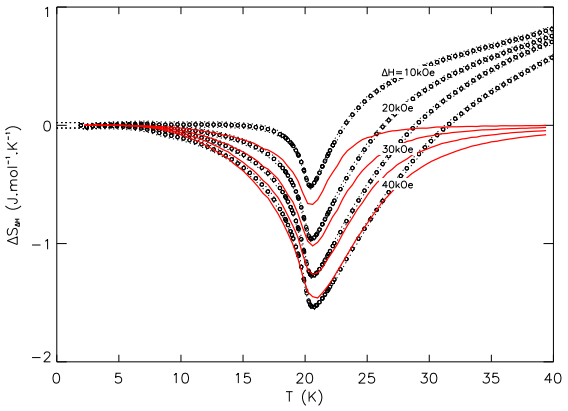

Figure 3. The isothermal MCE of $PrNiSi_2$ for different changes in the applied magnetic field (circles). The dotted lines enveloping the data shows the calculated margin of error. The solid lines show the MCE calculated from Eq.8.

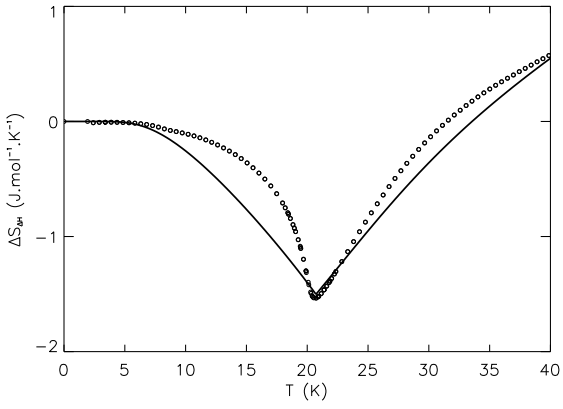

Figure 4. The MCE of $PrNiSi_2$ for $\Delta H = 40\,\mathrm{kOe}$ (circles) and the MCE calculated from Eq.9.

The isofield specific heat is used to calculate the isofield specific entropy $S_H(T)$ using

$$S_H(T) = \int_0^T \frac{C_{p,H}(T)}{T} dT. \tag{7}$$

The isothermal MCE is calculated from the specific entropy as $\Delta S_{\Delta H}(T) = S_H(T) - S_0(T)$ and shown in figure 3. The isothermal MCE in $PrNiSi_2$ shows features typical of the MCE close to a second order magnetic phase transition. In isotropic ferromagnetic compounds the isothermal MCE is negative, as increasing the applied field reduces the magnetic configurational entropy. The shape of the MCE in such systems is Caret-like, with an apex close to the transition temperature T_C [11]. However, contrary to the typical ferromagnetic MCE, the data in figure 3 shows a change in sign at temperatures well above T_C. In this region the MCE is positive and increasing with increasing temperature. For $\Delta H = 10\,\mathrm{kOe}$ this anomalous contribution increases to a point where it exceeds the magnitude of the negative apex value close to T_C.

The starting point for the analyses of the MCE shown in figure 3 is the Hamiltonian

$$\mathcal{H} = -g\mu_B B \sum_i J_{z,i} - \mathcal{J} \sum_i \sum_j J_{z,i} J_{z,j} \tag{8}$$

where $J_{z,i}$ denotes the z-component of the total angular momentum associated with site i. $\mathcal{J}$ is the isotropic exchange parameter (where exchange is restricted to nearest neighbours) while B denotes the magnetic field (assumed to be equal to $\mu_0 H$ as the moments are treated as test particles). The MCE is calculated from the above Hamiltonian using a simple Metropolis algorithm and a three-dimensional cubic $10 \times 10 \times 10$-element lattice. The calculation reproduces the $PrNiSi_2$ MCE for large $|\Delta H|$ as shown in figure 3. In the calculation it is assumed that $J_{z,i} = \pm 1/2$, $g = 1.50$ and $\mathcal{J} = 17.98k$ (here k denotes Boltzman's constant). This suggests that the $4f$-electron ground state in the system is a doublet.

A doublet ground state in $PrNiSi_2$ may arise due to two mechanisms, despite the orthorhombic CEF noted earlier. It is known that systems with CEF-induced non-magnetic singlet ground states may order through an exchange interaction if the exchange interaction is of the same order as the first putative CEF-excitation [12]. A second possibility, considered here, is that the O_n^0-terms in the CEF Hamiltonian are dominant.

The O_n^0 operator equivalents add terms of the form $\zeta J_{z,i}^n$ to the magnetic Hamiltonian (where $n = 2, 4$ and 6). Here ζ is a parameter controlling the relative strength of the CEF-term. As these contributions fall on the main diagonal, they serve to uplift the nine-fold degeneracy associated with the free ion multiplet while a description of the system in terms of the free-ion eigenstates is maintained. The degeneracy is not completely lifted however, as $|\pm J_{z,i}\rangle$ states, where $J_{z,i} \in \{-4, -3, ..., 3, 4\}$, have equal energy eigenvalues. These states are therefore doublets.

Restricting the O_n^0-terms to $n = 2$ yields the Hamiltonian

$$\mathcal{H} = -g\mu_B B \sum_i J_{z,i} - \mathcal{J} \sum_i \sum_j J_{z,i} J_{z,j} - \zeta \sum_i J_{z,i}^2 \tag{9}$$

where $J_{z,i} \in \{-4, -3, ..., 3, 4\}$. The assumption of O_2^0-dominance is consistent with uniaxial anisotropy, the latter usually appearing as a $AJ_{z,i}^2$ contribution to the magnetic Hamiltonian [13]. Accordingly it is assumed that ζ depends on the magnetic field orientation, subject to the constraint that ζ is maximum and larger than zero when the magnetic field is parallel to the z-axis. For the polycrystalline sample used here it is assumed that

$$\zeta = \begin{cases} 90k & \text{if} \quad B = 0 \\ 20k & \text{if} \quad B \neq 0. \end{cases} \tag{10}$$

In this sense, when $B \neq 0$ $\zeta = 20k$ is a weighted average over all possible crystal orientations. A mean-field calculation of the MCE under these assumptions is shown in figure 4 together with

the isothermal MCE calculated from the isofield specific heat of $PrNiSi_2$. With the addition of the angular dependence of ζ an anomalous component in the MCE appears above T_C. As is shown in the figure, the choice of values noted in Eq.10 quantitatively reproduces the MCE in $PrNiSi_2$. Therefore, a link is established between the change in sign of the MCE and the leading CEF-terms in the magnetic Hamiltonian.

4. Conclusion

The isothermal magnetocaloric effect in $PrNiSi_2$ shows a large positive increase with increasing temperature well above the magnetic phase transition. While the conventional negative MCE at lower temperatures is reproduced by a model Hamiltonian assuming a doublet ground state, the non-conventional component cannot be explained without the addition of an O_2^0-term to the model Hamiltonian. This term is consistent with uniaxial magnetic anisotropy, and its dependence on the magnetic field direction is shown to produce a similar positive MCE above T_C. This implies that the CEF-effects in $PrNiSi_2$ are dominated by the O_2^0-terms, which in turn explains the pressence of a doublet ground state in this system despite the point symmetry of the Pr^{3+}-sites in this structure.

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