

# Magnetic behaviour of the tetravalent praseodymium compound $\text{Sr}_2\text{PrO}_4$

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## Abstract

We report on investigations of the magnetic properties of the tetravalent praseodymium ( $\text{Pr}^{4+}$ ) compound  $\text{Sr}_2\text{PrO}_4$  by dc and ac magnetic susceptibility and heat capacity measurements. The compound shows signatures of long range magnetic order at  $T_N = 3$  K in the heat capacity and magnetization data. In addition, the temperature dependence of the field cooled and the zero-field cooled susceptibility is hysteretic below 10 K. Heat capacity versus temperature data show that a significant part of the magnetic entropy is released above  $T_N$ . This reveals that short range magnetic correlations among the Pr moments exist well above  $T_N$ . The magnetic entropy obtained from the heat capacity measurements indicates that only the crystal field ground state of Pr with effective spin- $\frac{1}{2}$  is significantly populated at low temperatures.

## 1. Introduction

Recently Fiscus and zur Loye [1] reported the formation of a new Pr based oxide material  $\text{Sr}_2\text{PrO}_4$ , where Pr was found to be in the 4+ state. Their crystallographic investigations showed that the material is isostructural to the inorganic blue phosphor  $\text{Sr}_2\text{CeO}_4$  with an orthorhombic crystal structure (space group *Pbam*). This structure consists of infinite chains of edge-sharing  $\text{PrO}_6$  octahedra separated by a network of  $\text{SrO}_6$  trigonal prisms. The  $\text{PrO}_6$  octahedra are slightly distorted with a difference in the Pr–O bond length along the axial and the equatorial directions in the octahedra.  $\text{Sr}_2\text{CeO}_4$  is not magnetically important as the  $\text{Ce}^{4+}$  ions do not carry any magnetic moment. On the other hand, the  $\text{Pr}^{4+}$  ions in  $\text{Sr}_2\text{PrO}_4$  are magnetic, with the preliminary investigations indicating that the compound undergoes long range magnetic order below  $T_N = 3$  K [1]. This compound is interesting because very few Pr-based oxides are known to contain tetravalent Pr ions. Secondly, the moment carrying Pr ions are structurally aligned in chains, which might give rise to interesting magnetic and electronic behaviour originating from low dimensional magnetic correlations along the chains.

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In this paper, we present the results of our investigations on the magnetic behaviour of Sr<sub>2</sub>PrO<sub>4</sub> by magnetization and heat capacity measurements.

## 2. Experimental details

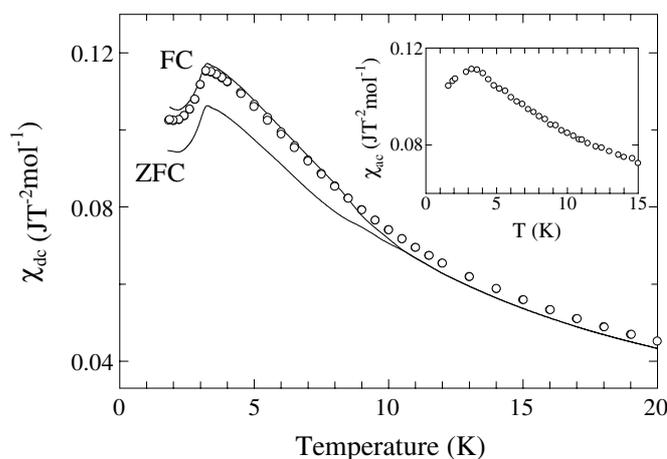
Polycrystalline samples of Sr<sub>2</sub>PrO<sub>4</sub> were prepared by solid state reaction, heating the starting materials (SrCO<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>) at 1000 °C in air [1]. The final sintering was carried out in a constant flow of oxygen gas for 12 h followed by a slow cooling (50 °C h<sup>-1</sup>) to room temperature. The room temperature x-ray diffraction data of the powder sample indicate that the sample has formed as a pure phase within the accuracy of this technique (typically the maximum volume of any undetected impurity phase is ~3%). The diffraction pattern can be indexed on the basis of an orthorhombic crystal structure (space group *Pbam*) with lattice parameters  $a = 6.111$  Å,  $b = 10.273$  Å and  $c = 3.587$  Å which compare well with those reported in the literature [1]. The isostructural nonmagnetic compound Sr<sub>2</sub>CeO<sub>4</sub> was also synthesized in order to determine the lattice contribution to the heat capacity. The dc magnetization ( $M$ ) measurements were carried out using a Quantum Design SQUID magnetometer in the temperature ( $T$ ) range 1.8–350 K. An Oxford Instruments vibrating sample magnetometer was used to measure the magnetic field ( $H$ ) dependence of the magnetization of Sr<sub>2</sub>PrO<sub>4</sub>. The ac susceptibility measurements were made using a standard mutual inductance method with an ac field of  $\mu_0 H \sim 10^{-4}$  T and a frequency of 403 Hz. The heat capacity data down to 1.8 K were obtained by a relaxation method using a Quantum Design Physical Properties Measurement System.

## 3. Results

The dc magnetic susceptibility ( $\chi_{dc} = M/\mu_0 H$ ) versus temperature data at  $\mu_0 H = 0.01$  T of Sr<sub>2</sub>PrO<sub>4</sub> are shown in figure 1. The data were collected for both zero-field cooled (ZFC) and field cooled (FC) conditions. Both the ZFC and the FC data show a peak in  $\chi_{dc}$  at 3.3 K, and a maximum in  $\frac{d(T\chi_{dc})}{dT}$  at 3 K with a temperature dependence that is typical of long range antiferromagnetic ordering. This peak in the susceptibility was also seen in an earlier study [1]. The susceptibility shows a tendency to level off (or even rise again at the low temperatures, particularly in the FC data) below 2.5 K. Similar features in the susceptibility behaviour below the ordering temperature have also been seen in other tetravalent Pr compounds such as Ba<sub>1-x</sub>Sr<sub>x</sub>PrO<sub>3</sub> [2]. In the case of Ba<sub>1-x</sub>Sr<sub>x</sub>PrO<sub>3</sub>, it was argued [2] that a ferromagnetic component associated with a canted antiferromagnetic spin arrangement could be responsible for this feature in the low temperature susceptibility. A similar argument can also be put forward for Sr<sub>2</sub>PrO<sub>4</sub>, although supporting neutron diffraction data are required to comment in detail on the nature of the magnetic phase which develops below 3 K. It should be mentioned here that, unlike the dc susceptibility data, our ac susceptibility measurement (see figure 1 inset) shows no anomalous upturn below 3 K.

Interestingly, in low applied fields ( $\mu_0 H < 0.1$  T) the temperature dependence of the FC and the ZFC dc susceptibility deviate from one other at  $T_{irr} = 10$  K, signifying that there may be an additional component in the magnetic behaviour of Sr<sub>2</sub>PrO<sub>4</sub> below this temperature. This hysteresis in the dc susceptibility ultimately disappears for an applied field above 0.1 T. For Sr<sub>2</sub>PrO<sub>4</sub>, we observe no anomaly in the ac susceptibility measurement around 10 K (see figure 1 inset).

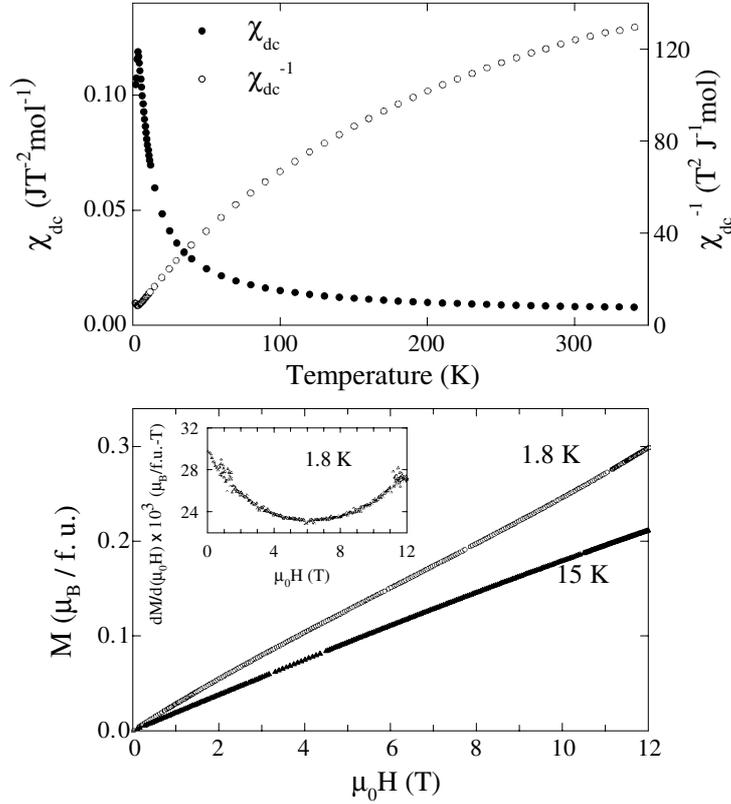
The magnetic susceptibility versus temperature data, measured up to 350 K, do not show simple Curie–Weiss behaviour (see figure 2). The inverse susceptibility is nonlinear and shows



**Figure 1.** The FC and ZFC susceptibility of Sr<sub>2</sub>PrO<sub>4</sub> as a function of temperature at an applied field of  $\mu_0 H = 0.01$  T (solid curves) and 0.1 T (open circles). It is to be noted that there is no irreversibility in the 0.1 T data. The inset shows the ac susceptibility (real part) versus temperature data measured in an applied ac magnetic field with an rms amplitude of  $\sim 10^{-4}$  T and a frequency of 403 Hz.

a negative curvature. In the previous report on Sr<sub>2</sub>PrO<sub>4</sub>, Fiscus and zur Loye identified a small temperature independent positive term in the susceptibility data as being responsible for the deviation from ideal Curie–Weiss behaviour. This additional contribution may occur when some energy levels, lying just above the ground state, become thermally populated over the temperature range of the measurement. The extra temperature independent contribution to the susceptibility arising from the mixing of the higher crystal field states is generally called the Van Vleck paramagnetism. The susceptibility can be expressed as  $\chi_{dc}(T) = C/(T - \theta_p) + \chi_0$ , where  $C$  is the Curie constant,  $\theta_p$  the paramagnetic Curie temperature and  $\chi_0$  the temperature independent part in the susceptibility. The best linear fit of the data  $1/(\chi_{dc}(T) - \chi_0)$  to  $T$  in the temperature range 150–350 K is obtained for  $\chi_0 = 5.52(6) \times 10^{-3} \text{ J T}^{-2} \text{ mol}^{-1}$  and the corresponding values of the effective moment and  $\theta_p$  are found to be  $0.93(2) \mu_B$  and  $-14(\pm 1)$  K respectively. The effective moment of Pr<sup>4+</sup> is much lower than the value of  $2.54 \mu_B$  expected for the  $4f^1$  state. A reduced value of the effective moment is observed in other compounds containing rare earth and actinide elements in an  $f^1$  state within an octahedral crystal field environment [3, 4]. This is related to the fact that, even at room temperature, higher energy crystal field states may not be fully populated. The observed  $\theta_p$  is much higher than the ordering temperature ( $\theta_p/T_N \sim 5$ ). This large value of  $\theta_p$  might be related to the observed irreversibility in the FC and ZFC susceptibility at  $T_{irr} = 10$  K, and suggests that a degree of magnetic frustration is present in the system well above  $T_N$ .

We have also collected isothermal magnetization versus field data (see figure 2) at different temperatures. The data at 1.8 K show a nearly linear behaviour up to field values of 12 T. A change in the curvature of the  $M$  versus  $\mu_0 H$  data is observed around  $\mu_0 H = 6$  T. The slope,  $dM/d(\mu_0 H)$ , at 1.8 K (see inset in the lower panel of figure 2) is always positive in the applied field range  $\mu_0 H = 0$ –12 T. However,  $dM/d(\mu_0 H)$  shows a minimum at around  $\mu_0 H = 6$  T, which signifies that the curvature of the  $M$  versus  $\mu_0 H$  data changes sign around 6 T. Above  $T_N$ , the  $M$  versus  $\mu_0 H$  data show a monotonic curvature, which is consistent with the expected Brillouin function behaviour in the paramagnetic state. This change in the magnetization below  $T_N$  at 6 T is probably related to a change in the spin orientation in the ordered state caused by the applied magnetic field. This phenomenon might be favoured by the

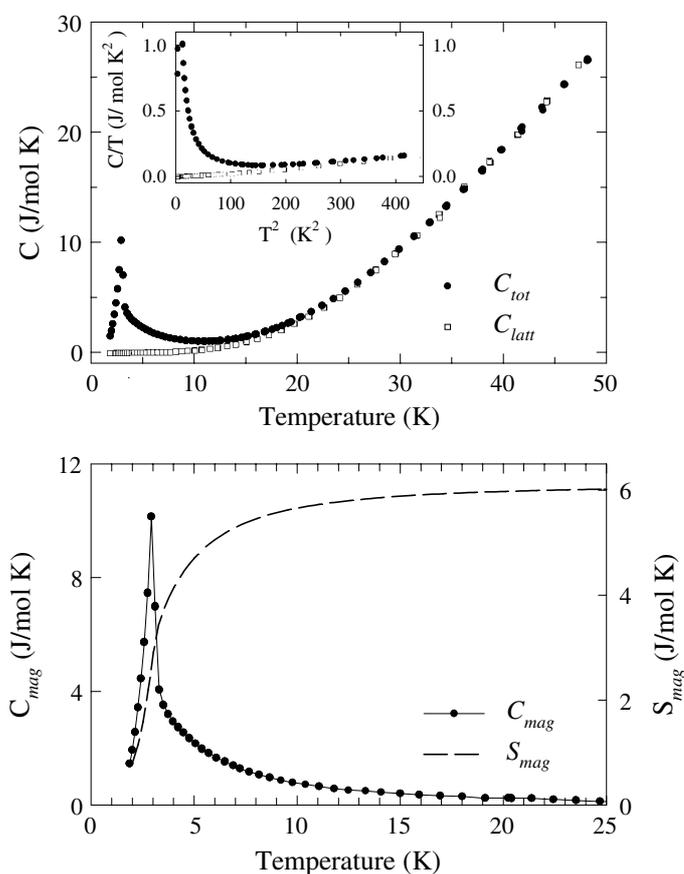


**Figure 2.** The upper panel shows the magnetic susceptibility versus temperature data in an applied field of 0.1 T. The lower panel shows the isothermal magnetization data as a function of the applied field at 1.8 and 15 K. The inset in the lower panel reveals the slope ( $dM/d(\mu_0 H)$ ) of the magnetization curve versus the applied field at 1.8 K.

fact that  $\text{Sr}_2\text{PrO}_4$  has strong anisotropy in its crystal structure, which can give rise to magnetic anisotropy in the system.

In order to obtain a more detailed view of the magnetic characteristics of  $\text{Sr}_2\text{PrO}_4$ , we have performed heat capacity measurements as a function of  $T$ . The data collected in the temperature range 2–50 K are shown in figure 3. Since the sample is an insulator, we have assumed that the total heat capacity of  $\text{Sr}_2\text{PrO}_4$ ,  $C_{\text{tot}}$ , is made up of two terms, a lattice contribution  $C_{\text{latt}}$  and a magnetic contribution  $C_{\text{mag}}$ . We have obtained  $C_{\text{latt}}$  from the heat capacity data of the non-magnetic isostructural compound  $\text{Sr}_2\text{CeO}_4$  with the necessary correction for the mass difference between Ce and Pr, made following the method of Bouvier *et al* [5]. Fitting the low temperature (2–30 K)  $C_{\text{latt}}$  versus  $T$  data to a simple  $T^3$  law provides a Debye temperature,  $\Theta_D = 437 \pm 4$  K. On the other hand,  $\Theta_D$  obtained by a full Debye integral fitting to the high temperature (200–350 K)  $C_{\text{tot}}(T)$  data of  $\text{Sr}_2\text{PrO}_4$  is found to be  $452 \pm 8$  K. The good agreement between these two  $\Theta_D$  values reinforces the view that the mass corrected heat capacity of  $\text{Sr}_2\text{CeO}_4$  provides a reliable estimate for the  $C_{\text{latt}}$  of  $\text{Sr}_2\text{PrO}_4$ .

The  $C_{\text{mag}}$  versus  $T$  data show a clear peak around 3 K, consistent with the results of the magnetization measurements. A significant fraction of the magnetic heat capacity is seen well above the ordering temperature with a tail extending up to around 25 K. This shows that a magnetic contribution to the heat capacity exists even at a temperature eight times higher



**Figure 3.** The top panel shows the total heat capacity ( $C_{tot}$ ) and the lattice contribution to the heat capacity ( $C_{latt}$ ) as a function of temperature for Sr<sub>2</sub>PrO<sub>4</sub>. The lower panel shows the temperature dependence of the magnetic contribution to the heat capacity ( $C_{mag} = C_{tot} - C_{latt}$ ) of Sr<sub>2</sub>PrO<sub>4</sub>. The magnetic part of the entropy ( $S_{mag}$ ) is also shown.

than the magnetic ordering temperature. The magnetic entropy ( $S_{mag}$ ), calculated from the heat capacity data (see figure 3), rises sharply up to 12 K and then tends towards the value of  $\sim 6 \text{ J mol}^{-1} \text{ K}^{-1}$ . Less than half of the measured magnetic entropy is released below  $T_N$ , whereas about 94% of the total measured entropy of  $6 \text{ J mol}^{-1} \text{ K}^{-1}$  is released below  $T_{irr}$ . A possible explanation for this large entropy release above  $T_N$  may be due to the existence of low lying crystal field states. However,  $C_{mag}(T)$  contains no Schottky-like anomaly typical of crystal field excitations at temperatures around  $T_{irr}$ . Given the fact that the dc susceptibility is irreversible below  $T_{irr}$ , it is more likely that the entropy tail corresponds to short range correlations between the Pr<sup>4+</sup> moments.

For a free Pr<sup>4+</sup> ion with one f electron ( $J = 5/2$ ), the Russel Saunders ground state can be denoted by  $^2F_{5/2}$ . In Sr<sub>2</sub>PrO<sub>4</sub>, the magnetic Pr<sup>4+</sup> ion is surrounded by oxygen atoms in an octahedral symmetry. The octahedral crystal field ( $O_h$ ) can break the  $^2F_{5/2}$  ground state into a  $\Gamma_7$  doublet and a  $\Gamma_8$  quartet [6]. For a doublet ground state  $S_{mag}$  is expected to be equal to  $R \ln(2S + 1) = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$ . The observed value of the magnetic entropy ( $S_{mag} \approx 6 \text{ J mol}^{-1} \text{ K}^{-1}$ ) indicates that at low temperatures (below 30 K) only the  $\Gamma_7$  doublet with an effective spin- $\frac{1}{2}$  is populated.

#### 4. Discussion

Our magnetization and heat capacity measurements establish that the material  $\text{Sr}_2\text{PrO}_4$  undergoes long range magnetic order at  $T_N = 3$  K. The large value of the magnetic heat capacity above  $T_N$ , the irreversibility in the dc susceptibility at  $T_{\text{irr}} = 10$  K and the high value of  $\theta_p$  as compared to  $T_N$  indicate that magnetic correlations exist at temperatures higher than  $T_N$  and that there may be a degree of magnetic frustration in the system. The large magnetic contribution to the heat capacity seen well above  $T_N$  cannot be due to a small amount of extra phase which escapes detection in our x-ray diffraction measurements. We have investigated several batches of the samples with different heat treatments and we find no difference in the extent and nature of the irreversibility in the susceptibility data at 10 K. In order to exclude the possibility that a small amount of Pr oxide impurity gives rise to the hysteresis observed at  $T_{\text{irr}}$ , we have also measured the susceptibility of the starting material  $\text{Pr}_6\text{O}_{11}$  after subjecting it the same heat treatment as that of the sample. No anomaly was observed around 10 K.

Given the fact that  $\text{Sr}_2\text{PrO}_4$  possesses a chain structure, it is possible that intra-chain spin correlations may be responsible for the magnetic anomaly at  $T_{\text{irr}}$  in the system. We also find that a large fraction of the magnetic entropy is released between  $T_{\text{irr}}$  and  $T_N$ , which is consistent with the development of spin correlations along the chains [7]. The negative value of  $\theta_p$  suggests that the correlations along the chain are antiferromagnetic in nature. The inter-chain distance between two Pr ions is about twice the intra-chain distance. The weakly coupled spin chains ultimately attain a full three-dimensional ordering below 3 K. A low dimensional spin arrangement prior to the onset of three-dimensional long range order has been reported for several spin chain systems [8]. An investigation on a single-crystal sample of  $\text{Sr}_2\text{PrO}_4$  is necessary in order to confirm the presence of low dimensional magnetic effects in this system. Furthermore, in order to better understand the nature of the long range magnetic order at  $T_N$ , the heat capacity investigations should be extended below 2 K.

#### Acknowledgment

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