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Magnetic ordering in hexagonal PrCuSi

A M Strydom and B M Sondezi-Mhlungu

Physics Department, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa
E-mail: amstrydom@uj.ac.za

Abstract. We report on the first multi-parameter investigation of a well-characterized sample of PrCuSi. The crystal structure is hexagonal, with a unique lattice site for each of the 3 atoms. Specific heat measurements indicate long-range magnetic ordering, and data of magnetic susceptibility confirm a paramagnetic-to-antiferromagnetic type transition at \( T_N = 5.1 \) K, in contrast to what was claimed previously in exploratory work on this compound. There is a well-defined anomaly in the electrical resistivity \( \rho(T) \) at \( T_N \), below which a spin-density-wave expression accurately accounts for \( \rho(T) \) according to AFM ordering. A field-driven instability of the ordered state is furthermore indicated by a sharp feature in \( \rho(B) \) at \( B = 0.75 \) T.

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1. Introduction
The ternary, equiatomic class of compounds designated by \( \text{RE-T-M} \) (\( \text{RE} = \) rare-earth element, \( T = \) group VIII or IB d-electron element, \( M = \) p-electron element) offer one of the simplest crystal structure types with which to study rare-earth magnetism. They comprise a wide variety of magnetic properties and enable systematic studies of, amongst others, the influence of the valence electron count, state of hybridization of the local f-electron orbital, and interplay between f-electron and d-electron magnetism. Compounds in the \( \text{RECuSi} \) subclass have the feature of forming in an atomically ordered hexagonal crystal structure which negates, in principle, the ambiguity that may arise from multiple or competing magnetic interactions when the magnetic ion occupies two different lattice sites. There are at present a total of 15 Pr-based silicides \( \text{PrTSi} \) and germanides \( \text{PrTGe} \). Among these, magnetic ordering is a rare occurrence, with only \( \text{PrRuSi} \) \( (T_N = 73 \) K [1]), \( \text{PrRuGe} \) \( (T_N = 62 \) K [1]), \( \text{PrCuSi} \) \( (T_C = 14 \) K [2]) and \( \text{PrCuGe} \) \( (T_N = 1.8 \) K [3]) having been reported to show a zero-field magnetically ordered ground state. The subject of this work is PrCuSi. Our results show compelling evidence for antiferromagnetic ordering - in contrast to what was previously reported on this compound [2]. We also found a field-instability of the ordering which appears to originate from a spin rearrangement.

2. Experimental
A polycrystalline ingot of PrCuSi was prepared by arc-melting stoichiometric quantities of the elements (purity in weight-%) Pr (99.99), Cu (99.995), and Si (99.9999) in zirconium-gettered ultra-high purity argon. This was followed by annealing for 7 days at 750°C. The sample thus obtained was checked by wavelength dispersive x-rays from which an elemental composition of
PrCu$_{1.01(3)}$Si$_{1.027(8)}$ was determined. The results of powder x-ray diffraction of the PrCuSi sample are shown in Fig. 1. A Rietveld refinement fit to the data yields lattice parameters of $a = 4.2218(1)$ Å and $c = 7.9024(1)$ Å in the hexagonal $P6_3/mmc$ space group. The values compare closely with the work of Iandelli et al [4], who also established that atomic ordering may be achieved in a number of RE$_2$CuSi compounds by annealing that modifies the generic AlB$_2$ structure type into the ordered Ni$_2$In phase. The fixed atomic coordinates used in the refinement are as follows: 2Pr: 2$a$ (000), 2Cu: 2$c$ ($\frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{2}$), and 2Si: 2$d$ ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$).

All the remaining physical properties reported in this work were measured on a commercial PPMS station from Quantum Design (San Diego), and magnetic data were collected on an MPMS equipped with a SQUID magnetometer from the same manufacturer.

The magnetic susceptibility $\chi(T)$ of a solid specimen of PrCuSi shows paramagnetic behaviour below 400 K, and the least-squares straight-line fit of the Curie-Weiss law to the data depicted in the main panel of Fig. 2 yields a Weiss temperature of $\theta_p = -11.0(5)$ K and an effective moment of $\mu_{\text{eff}} = 3.88(1)$ $\mu_B$. This is a reasonable approximation of the Hund’s rule free-ion expectation value of 3.58 $\mu_B$ for Pr$^{3+}$. We used an applied field of 0.1 T for the $\chi(T)$ measurement, in which $\chi(T) = \partial M/\partial B|_{B=0.1}$ T (see further below) was ascertained to be field-independent. The temperature-dependent susceptibility starts deviating from non-interacting behaviour below about 100 K, which is likely due to structure in the 4$f$–electronic levels brought about by the action of a crystal-electric field. At 5.1(1) K, $\chi(T)$ reaches the apex of a sharp peak. This is characteristic of long-range antiferromagnetic order in the sample. We note that there are no detectable signs in our susceptibility measurements of the ferromagnetic order that was reported previously for PrCuSi at 14 K [2].

Above the Néel ordering in PrCuSi, its magnetization shows only weak curvature (see $T = 8$ K isotherm in Fig. 3). Up to 0.5 T, the low-field magnetization of this isotherm coincides with the 2 K magnetization in the ordered region until, at 0.7 T, the 2 K isotherm rises abruptly in a metamagnetic-like fashion. Even in 5 T the magnetic response falls far short of the $gJ = 3.2$ $\mu_B$ saturation moment of Pr, although it is unlikely that a field of 5 T would overcome the entire crystal-electric field splitting of nine $J = 4$ levels.

Fig. 4 shows a semi-log plot of the specific heat of PrCuSi (round symbols). Near the antiferromagnetic order a sharp anomaly is found that reaches up to $C_p = 26$ J/mol-K. The specific heat of the nonmagnetic reference compound LaCuSi is also shown for comparison (square symbols). We approximate the lattice heat capacity of PrCuSi with that of the nonmagnetic, isostructural compound LaCuSi by way of their comparable molar masses and
Figure 2. Magnetic susceptibility of PrCuSi, with least-squares fit of a Curie-Weiss law (red line). The measurements were taken in a field-cooling mode. Inset: Susceptibility at low temperatures, showing the antiferromagnetic order at $T_N = 5.1(1)$ K.

Figure 3. Magnetization data of PrCuSi collected below ($T = 2$ K) and above ($8$ K) the Néel ordering temperature of $T_N = 5.1$ K. The arrow marks a metamagnetic jump, nearly doubling the magnetization, that occurs in the ordered region at a field of $B_{\text{meta}} = 0.7$ T.

electronic structures, which allows calculation of the effective 4f-derived specific heat of PrCuSi as well as its magnetic entropy (see blue dashed line in Fig. 4). The entropy released at $T_N$ amounts to $\sim 0.7 \, R \ln 2$.

The electrical resistivity $\rho(T)$ of PrCuSi is shown in Fig. 5. We note that $\rho(T)$ has an overall metallic character, but for brevity only the low-temperature behaviour is shown. The approach to magnetic ordering increases $\rho$ below about 7 K, before a well-defined peak marks $T_N$. This is followed by a rapid decrease in $\rho(T)$ which suggests the freezing of a large component of spin-disorder scattering. The red symbols depict measurements in a field of 0.5 T, i.e. slightly below the metamagnetic field of 0.7 T. Whereas the increase in $\rho$ immediately above $T_N$ is no longer evident in this field, below $T_N$ $\rho(B = 0.5$ T) traces the zero-field data almost exactly. The dashed line depicts a least-squares fit to the zero-field $\rho(T,B = 0)$ data of the prediction [5] for scattering of electrons from antiferromagnetic magnons governed by a dispersion relation $\omega^2 = \Delta^2 + Dk^2$:

$$\rho(T) = \rho(T = 0,B = 0) + A\Delta^{3/2}T^{1/2}\left[1 + \frac{2}{3}T\Delta + \frac{2}{15}\left(\frac{T}{\Delta}\right)^2\right] \exp\left(-\Delta/T\right) .$$

The fit yields a residual resistivity $\rho(T = 0,B = 0) = 16.15(5) \, \mu\Omega\cdot\text{cm}$, a prefactor $A = 0.34(5) \, \mu\Omega\cdot\text{K}^{-2}$, and a spin-wave energy gap of $\Delta/k_B = 16(1)$ K. In the inset of Fig. 5, the field dependence of resistivity ($T = 2$ K) is shown in the form $\rho(T = 2,B)/\rho(T = 2,B = 0)$. Here, the effect of a magnetic field on $\rho$ is seen much more dramatically by a sharp drop in $\rho$ right at $B = B_{\text{meta}}$.

3. Discussion

Our work on a well-characterized sample proves antiferromagnetic order in PrCuSi below $T_N = 5.1$ K. The ordering comprises Pr ions having a stable Hund’s rule Pr$^{3+}$ moment at higher temperatures which occupy a single lattice site sandwiched between Cu-Si layers. Specific heat and resistivity at $T_N$ have the signatures of a first-order transition, with the presence of strong
Figure 4. Left-hand scale: Semi-log plot of the specific heat of PrCuSi (circles) and LaCuSi (squares). Right-hand scale: Dashed blue line showing the calculated magnetic entropy $S_{4f}(T)$ of PrCuSi in units of $R \ln 2$.

Figure 5. Main panel: Electrical resistivity of PrCuSi in zero field (black) and in a field of 0.5 T (red). Inset: Magnetoresistance MR, in the form $\rho(B)/\rho(0)$, against field. $B_{meta}$ signals an abrupt decrease in MR.

magnetic fluctuations quenched by an applied field of 0.5 T (see Fig. 5).

The magnetization of PrCuSi suggests furthermore that the nine-fold multiplet of the Pr$^{3+}$ ion is split by a crystal-electric field interaction. In hexagonal point symmetry, the splitting is expected to result in three non-magnetic singlets $\Gamma_1$, $\Gamma_3$, and $\Gamma_4$, plus three doublet states $\Gamma_{5a}$, $\Gamma_{5b}$, and $\Gamma_6$. In spite of the fact that the ordering at $T_N$ releases significantly less entropy than that of a doublet state, one may reasonably expect magnetic correlations immediately above $T_N$ to incorporate part of the magnetic entropy. The electrical resistivity (Fig. 5) rises below about 7 K already, and thus supports this conjecture. Considering our magnetization data of PrCuSi, calculations [6] of a $J = 4$ rare-earth ion in an hexagonal crystal field suggest that at least one doublet state must be involved in the ground state of PrCuSi.

The magnetic ordering is found not to be stable in an applied field. With the data at hand, the antiferromagnetic nature of the ordering is judged to be retained in small fields up to 0.7 T, beyond which a ferromagnetic or co-linear spin arrangement appears to be the most likely description.

Work is in progress to map the $B - T$ phase diagram of PrCuSi more accurately. Neutron diffraction measurements, also in fields, are highly desirable to resolve the magnetic structure and its field-driven rearrangement in PrCuSi.

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