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$CePd_2Si_2$: A REDUCED-MOMENT ANTIFERROMAGNET

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The compound $CePd_2Si_2$ has been investigated by neutron scattering, DC-susceptibility, specific-heat and resistivity measurements. $CePd_2Si_2$ crystallizes in the tetragonal I4/mmm structure. Below 8.5 K antiferromagnetic ordering takes place in a pattern consisting of ferromagnetic (110) planes with the spins perpendicular to the planes and alternating orientation in adjacent planes. The reduction of the Ce-moment from 2.55(5) μ_B for $T \geq 125$ K to .66(6) μ_B at 4.2 K is larger than expected on basis of crystal-field calculations. The extra reduction is ascribed to a partial Kondo screening of the Ce-moments. An additional indication for partial screening comes from specific-heat measurements, which give a slightly enhanced value for the parameter γ (65(2) mJ/mol.K^2). Resistivity measurements revealed a large anisotropy between a- and c-axes. In the neutron scattering experiments no critical scattering was observed, although the temperature dependence of the staggered magnetisation (critical exponent β = .37(3)) indicates a second-order phase transition at 9.2(5) K. We conclude that $CePd_2Si_2$ is a reduced-moment antiferromagnet with a Kondo temperature $T_K > T_N$.

1. Introduction

Since the discovery of the heavy-fermion behaviour of $CeCu_2Si_2$ by Steglich et al.[1], many other RT_2Si_2-compounds, with R=Ce or U, and T a 3d-, 4d- or 5d-transition metal have been investigated. In a systematic review Palstra et al.[2] have pointed out a trend from Pauli paramagnetic behaviour to (strong) local-moment behaviour for an increasing number of d-electrons. If we correlate the number of d-electrons with the inverse of the coupling constant J between the localized Ce moments and the conduction electrons, the trend mentioned above can be explained from a model proposed by Doniach[3] and further developed by Lawrence[4]. Doniach compared the energy of a Kondo singlet with that of an RKKY-antiferromagnetic ground state, both as a function of J. For small J the RKKY-state has the lowest energy, while the Kondo-singlet state is favoured for large J. For intermediate J values, the Kondo- and RKKY-interaction are of comparable magnitude, and a complex behaviour may be expected. According to Doniach, the one-dimensional Kondo lattice exhibits a second-order phase transition at T=0 and $J=J_c$ between the antiferromagnetic RKKY-state and the Kondo-like state. For $J>J_c$ there is an energy gap (the singlet-triplet splitting), which will tend to zero for $J \to J_c^+$, leading to large spin fluctuations. The second-order character of the transition implies that for $J \to J_c^-$ the system will be antiferromagnetic with very small local moments, even though the localized f-electrons are in a state with a well-defined non-zero spin.

A likely candidate for such reduced-moment antiferromagnetic behaviour is $CePd_2Si_2$. Neutron powder diffraction experiments showed an antiferromagnetic transition at T_N=10.5 K, with an effective Ce-moment of .62 μ_B.[5] Suceptibility[6-9], resistivity[6] and specific-heat measurements[9], all performed on polycrystalline samples, revealed the presence of large spin fluctuations, but in some of them[7,8] the transition to antiferromagnetic order was not observed. Both resonant photoemission[10] and thermopower[11] measurements showed that $CePd_2Si_2$ is probably close to the transition regime between antiferromagnetic and Kondo-lattice systems.

To resolve the discrepancies between some of the previously reported results, we have performed a systematic investigation of $CePd_2Si_2$ by neutron diffraction, DC-susceptibility, resistivity and specific-heat measurements. Most of our measurements were carried out on single crystals, firstly to reduce the influence of possible impurities or second phases in the

sample, secondly to study the anisotropy in the DC-susceptibility and resistivity.

2. Experimental Results

2.1. Crystallographic and Magnetic Structure

For the neutron powder diffraction experiments a sample was prepared from a stoichiometric melt of the three constituents. After powdering, the sample was annealed for two hours at 500°C. The diffractogram was recorded on the powder diffractometer HB5 at the High Flux Reactor at Petten. A wavelength of 2.5791 Å was used in combination with 30' Soller collimators placed between the reactor and monochromator and between sample and detectors. Higher-order beam contamination was eliminated by means of a pyrolytic graphite filter. The data were analysed with the Rietveld profile refinement technique[12], using nuclear scattering lengths of $.484 \times 10^{-12}$ cm for Ce, $.415 \times 10^{-12}$ cm for Si, and $.591 \times 10^{-12}$ cm for Pd. The magnetic formfactor for Ce^{3+}, used in the refinement of the data collected at 4.2 K, was taken from ref. 13. A few weak impurity lines in the diagrams could be attributed to PdO.

$CePd_2Si_2$ appears to crystallize in the body-centred tetragonal $ThCr_2Si_2$ structure (I4/mmm) with Ce at (000), Pd at ($\frac{1}{2}$ 0 $\frac{1}{4}$) and Si at (0 0 z). An overall isotropic Debye-Waller factor was used. The occupation numbers for the Pd and Si sites refine to 1 within twice their standard deviation, indicating that interchange between Pd and Si ions does not occur. The structural parameters at 293 K and 4.2 K are given in table I and a typical fit is shown in Fig. 1.

At 4.2 K three weak additional lines are observed (inset Fig. 1), which can be indexed as the ($\frac{1}{2}$ $\frac{1}{2}$ ℓ)-reflections with ℓ = 1, 2, 3. The absence of the ℓ=0 reflection together with the propagation vector $\vec{q}$ = ($\frac{1}{2}$ $\frac{1}{2}$ 0) give an antiferromagnetic structure as shown in Fig. 2. There are two domain types with ferromagnetic (110) or ($1\bar{1}0$) planes, the spin being perpendicular to these planes. The calculated moment is 0.66(6) μ_B (R_{magn} = 36.5%). These results are in agreement with earlier work by Grier et al.[5]

It should be noted that the diffraction data do not allow a distinction between a non-collinear $2\vec{q}$ structure and two equally populated collinear domain types. However, the collinear structure is favoured by the RKKY-interaction (see Sec. 3) and is therefore considered to be the most probable one.

We also measured the intensity of the magnetic ($\frac{1}{2}$ $\frac{1}{2}$ 1)-reflection as a function of temperature on a single crystal, prepared with a modified tri-arc Czochralski method[14]. These measurements were performed on spectrometer HB1 at a neutron wavelength of 2.655 Å. A pyrolytic graphite filter was used to reduce the second-order beam contamination and 30' Soller collimators were placed between monochromator and sample and between the sample and detector. The variation with temperature of the integrated ($\frac{1}{2}\frac{1}{2}$1) intensity derived from scans // [001] is characteristic of a second-order phase transition (cf. Fig. 3). Fitting the data to the power law $I = A\varepsilon^{2\beta}+B$ with $\varepsilon = (T_N-T)/T_N$ and 4 adjustable parameters yields values T_N = 9.2(5) K and β = 0.37(3) for the critical temperature and exponent. The constant background consists mainly of the nuclear (112) reflection of $\lambda/2$ neutrons. Even very close to T_N ($\varepsilon = 2\times10^{-3}$) there is no indication for critical magnetic scattering at the Bragg position ($\frac{1}{2}\frac{1}{2}$1) and at the points $\vec{Q}$ = ($\frac{1}{2}$,$\frac{1}{2}$,0.948) and (0.477,0.477,1).

2.2. DC-Susceptibility

The DC-susceptibility was measured on a single crystal with a vibrating sample magnetometer operating at 21 Hz with a static field H = 2 T along the [100]-, [110]- and [001]-direction of the crystal.

The experimental results for χ[100] and χ[110] clearly show the antiferromagnetic transition at 8.5(5) K (see the inset of Fig. 4), but the preferred spin orientation is not obvious. The typical $\chi_\perp$-behaviour observed for H// [110] is in contrast with the expected combination of $\chi_{//}$ and $\chi_\perp$ from the domains with spins along [110] and [$1\bar{1}0$], respectively. One may conclude that the field of 2T is large enough to flip the spins in the former domain type to the [$1\bar{1}0$] direction. When the field is oriented along [100], spin flip will not occur because the [110]- and [$1\bar{1}0$] directions remain equivalent, and a superposition of $\chi_{//}$ and $\chi_\perp$-behaviour is observed.

At temperatures above 125 K $CePd_2Si_2$ exhibits a Curie-Weiss behaviour with θ_{cw} = -55(2) K along the a-axis and -16(2) K along the c-axis, and an effective moment of 2.55(5) μ_B per formula unit.[2] The Néel temperature of 8.5(5) K is about 20% lower than the values deduced earlier [6,9,11] from susceptibility measurements on polycrystalline samples.

2.3. Resistivity

Resistivity measurements were performed on bar-shaped samples of 1x1x3 mm³ dimension along the a- and c-axis, using a four-point probe method. The voltage- and current leads were attached to the samples with silver paint DAG1415. The relative accuracy is about 0.1%, the absolute values are correct within 10% due

Table 1. Results of the neutron powder diffraction data refinements. The standard deviations based on statistics are given in parentheses.

$R_n = 100.\sqrt{\Sigma(I_n(obs) - \frac{1}{c} I_n(calc))^2 / \Sigma I_n(obs)}$

T(K)	a(Å)	c(Å)	z	B(Å^{-2})	R_n(%)
293	4.2388(1)	9.8889(4)	.3790(1)	.50(5)	2.5
4.2	4.2214(2)	9.8960(6)	.3806(2)	.16(6)	3.9

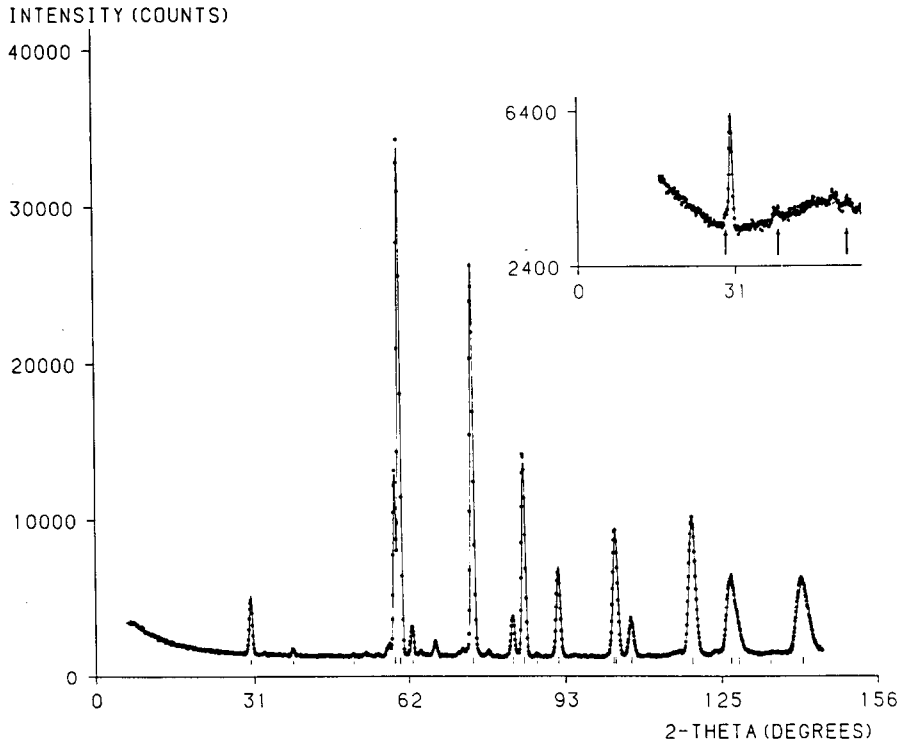

Fig. 1. Neutron diffraction pattern for $CePd_2Si_2$ obtained at 293 K. The full line represents the fit to the data. The positions of the nuclear reflections are indicated at the bottom of the diagram. In the inset three additional weak magnetic reflections at 4.2 K are indicated by arrows. The magnetic ($\frac{1}{2}$ $\frac{1}{2}$ 1) reflection is overlapped by the stronger nuclear (002) reflection.

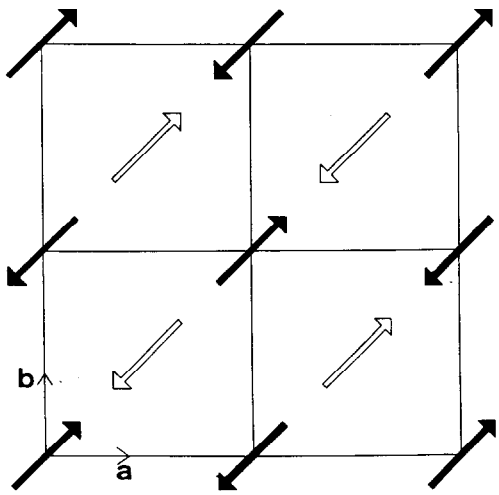

Fig. 2. Spin configuration in one of the domain types in $CePd_2Si_2$, deduced from the neutron diffraction experiments at 4.2 K.

to uncertainties in the dimensions of the sample. We observed a large anisotropy between the a- and c-axes (Fig. 5). The antiferromagnetic transition at 8.5(5) K is clearly seen; $d\rho/dT$ is negative for temperatures just above T_N in spite of the absence of critical scattering in the neutron experiments. Note also the broad maximum at 100 K, due to crystal fields. These results are qualitatively in agreement with measurements on polycrystalline samples by Murgai et al.[6]

2.4. Specific Heat

Specific-heat measurements were carried out on a single crystal, using the pulsed heating method. The entropy change due to the magnetic transition at 8.5(5) K was calculated to be .28 R, which is about 40% of Rln2. The linear coefficient γ, as deduced from the C/T versus T^2 plot (Fig. 6) is 65(2) mJ/mol.K^2, while the Debye temperature is estimated as 244(5) K. The present value of γ is about 50% smaller than the one reported by Dhar et al.[9] for a polycrystalline sample.

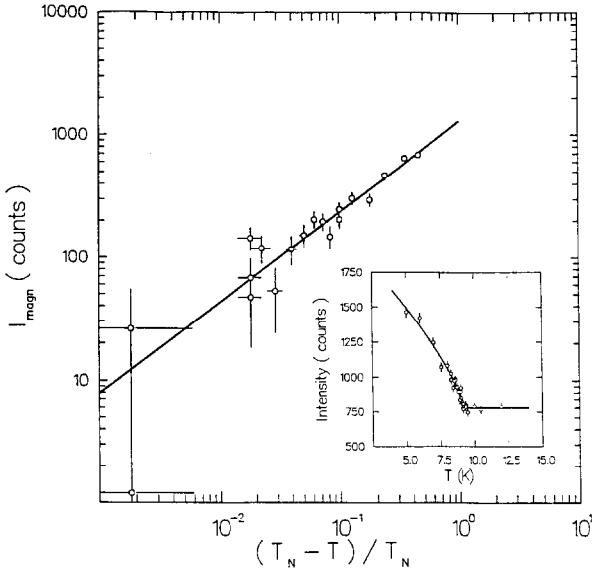

Fig. 3. Temperature dependence of the integrated intensity of the magnetic ($\frac{1}{2}$ $\frac{1}{2}$ 1) reflection near the ordering temperature T_N. The full line represents a power-law fit to the data as described in the text. The inset shows the measured integrated intensities as a function of temperature.

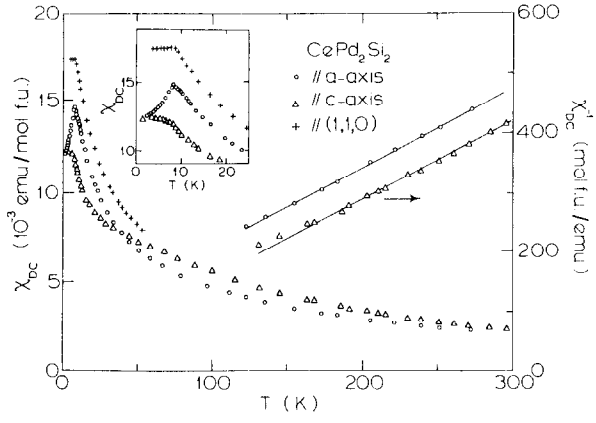

Fig. 4. Temperature dependence of the DC-susceptibility and inverse susceptibility of single crystalline $CePd_2Si_2$ along several directions.

3. Discussion

The neutron diffraction experiments on $CePd_2Si_2$ at 4.2 K reveal a large reduction of the local Ce moment to 0.66 μ_B in the antiferromagnetically ordered state. By comparing this value with those found in similar systems, ranging from 1.2 to 1.5 μ_B/atom[5,16] and with the results of crystal-field calculations for $CeCu_2Si_2$ (1.2 μ_B/Ce-atom)[15], we conclude that

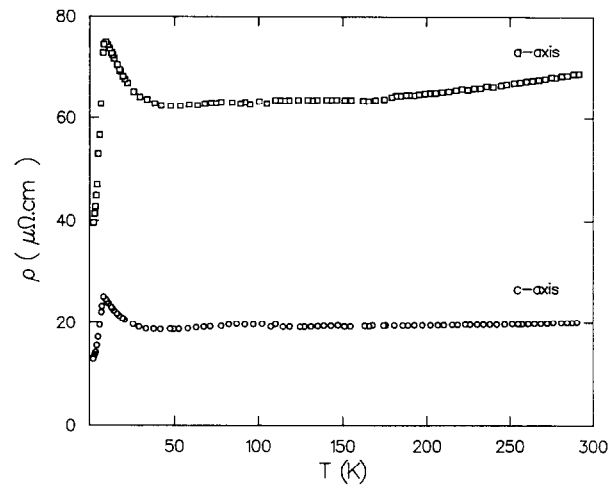

Fig. 5. Temperature dependence of the resistivity of $CePd_2Si_2$ measured along the a- and c-axis.

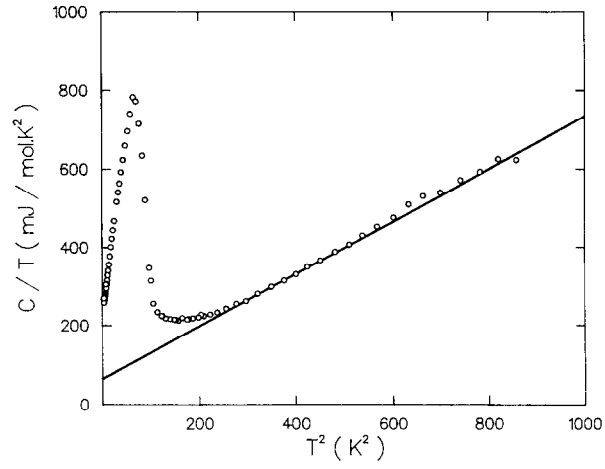

Fig. 6. Specific heat of $CePd_2Si_2$ plotted as C/T vs. T^2 yielding γ.

this reduction cannot be explained from crystal-field effects alone. We therefore suggest that $CePd_2Si_2$ is within the transition regime between antiferromagnetism and the Kondo-lattice phase as explained in the introduction. In that case the Kondo spin fluctuations are responsible for the extra moment reduction.

The low value of the effective Ce-moment might be the reason why no critical scattering was observed, in spite of the second-order phase transition at T_N with the accompanying spin fluctuations. The critical exponent β = .37(3) is in accordance with renormalisation-group predictions for 3D model systems, and definitely rules out a mean-field behaviour as proposed by Grier et al.[5]

Additional evidence for the presence of spin fluctuations and crystal- field effects is the double-bump structure observed in the resistivity. The same kind of behaviour is found in

$CeCu_2Si_2$, where spin fluctuations and crystal-field effects are of equal importance.[17] This phenomenon is known as the so-called "Kondo sideband resonances".[18] In $CePd_2Si_2$, however, this behaviour is cut off by the antiferromagnetic transition at 8.5 K.

The specific-heat measurements also show the onset of Kondo screening through the slight enhancement of the value for γ (65 mJ/mol.K^2). The entropy change is small with respect to Rln2, which indicates that the groundstate, Γ_7, of Ce is strongly perturbed, which may again be due to hybridisation and Kondo spin fluctuations.

The antiferromagnetic ordering pattern for $CePd_2Si_2$ as obtained from neutron scattering and confirmed by DC-susceptibility measurements, can be explained from the anisotropy of the RKKY-interaction, which favours the formation of antiferromagnetically coupled ferromagnetic planes with spins perpendicular to the planes[19]. This planar anisotropy is also responsible for the difference in the extrapolated χ (T=0) values for the field directions parallel to the [001]- and [110]-direction, respectively. The preferred directions of the spins, parallel to $[1\bar{1}0]$ or $[\bar{1}10]$, might be due to the crystal fields in $CePd_2Si_2$. It appears from a simple calculation that in a tetragonal field the Γ_7 groundstate is affected by other states (in an internal or external magnetic field) and that the maximum magnetic moment is either along the [001] or along the [110] direction, depending on the sign of the second-order terms of the crystal-field Hamiltonian. Note that in many similar Ce-compounds the moments are direct along [001] in the ordered state.

We conclude that at least three effects are important in $CePd_2Si_2$: the crystal-field effects, the Kondo spin fluctuations and the RKKY-interaction. For $T \gtrsim 125$ K $CePd_2Si_2$ exhibits a Curie-Weiss behaviour with effective Ce-moments of 2.55 μ_B/atom. At intermediate temperatures (8.5 K $\lesssim T \lesssim$ 125 K) the Kondo spin fluctuations are dominating, leading to an extra reduction of the magnetic moment. This reduced moment is "frozen in" below T_N=8.5 K, where the RKKY-interaction takes over the leading role, which results in an antiferromagnetically ordered state with very small effective moments.

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