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Published in:
Journal of Physics-Condensed Matter

Citation for published version (APA):
Determination of the crystal-field parameters for CePtSn

M Diviš†, H Nakotte†, F R de Boer‡, P F de Châtel‡ and V Sechovský†
† Charles University, Department of Metal Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
‡ University of Amsterdam, van der Waals–Zeeman Laboratory, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Received 22 March 1994, in final form 23 May 1994

Abstract. We have determined a set of crystal-field parameters for CePtSn which accounts for the available susceptibility, high-field magnetization at 4.2 K and inelastic neutron-scattering data. The analysis of experimental data revealed that the single-ion approach is reliable mainly at high temperatures (T > TN, TK) or at high magnetic fields where the energy associated with the exchange and coherence effects is much lower.

1. Introduction

Among the cerium intermetallic compounds, the equiatomic ternary systems CeTX (T = transition metal; X = p metal) are currently receiving wide scientific interest and they are the subject of systematic investigations [1]. In particular, CePtSn was classified as a 'metallic Kondo compound', which orders antiferromagnetically at 7.5 K [2]. A previous investigation on a single crystal of CePtSn has revealed strong anisotropy of the magnetic and transport properties and an attempt was made to construct the magnetic phase diagram [3]. The anisotropy of the magnetic susceptibility was successfully described by suitable chosen parameters in the microscopic crystal-field (CF) Hamiltonian, but the deduced CF level splitting of the 2F5/2 multiplet (Δ1 = 304 K; Δ2 = 573 K) does not agree with the results of recent inelastic neutron-scattering (INS) experiments, which provide values of Δ1 = 273 K, Δ2 = 425 K [4] or Δ1 = 278 K, Δ2 = 405 K [5].

On the other hand, the precise determination of CF parameters is highly desirable in order to enable a quantitative interpretation of transport properties and the low-temperature properties in general. The single-ion approach of CF theory is bound to break down at low temperatures, where the coherence and magnetic ordering effects prevail. The periodic Anderson model (see, e.g., [6, 7]), involving the lowest CF doublet, is likely to give the best description in this regime. The nature of this doublet involved in this description is determined by the CF Hamiltonian, which, in turn, can be established by analysing some of the physical properties in high magnetic fields and at high temperatures, where the single-ion approach is adequate. In this paper, we therefore present a full analysis of published magnetic data, specific-heat and INS measurements in order to determine a consistent set of CF parameters.

2. Method of analysis

The high-temperature (T > TN; TK ≈ 10 K) properties of CePtSn are governed by a strong CF interaction which splits the 4f-electron states of the Ce3+ ion [3]. The environment
of the Ce site has approximately $C_{6h}$ point symmetry if the approximate space group $Pnma$ is used instead of the correct orthorhombic space group $Pn2_1a$ [8]. To keep the number of the adjustable parameters in the CF Hamiltonian to a minimum, we assume orthorhombic symmetry of the CF interaction used by Takabatake et al [3]. The microscopic CF Hamiltonian of the required orthorhombic symmetry is usually written in the Stevens parametrization scheme [9];

$$\mathcal{H}_{\text{CF}} = B_2^0 O_2^0 + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4$$

(1)

where $B_{2/4}^M$ are the CF parameters, which describe the strength of the interaction, and $O_{2/4}^M$ are the operator equivalents. In the following, we shall determine the values of the CF parameters by an analysis of experimental data. For this purpose, it is convenient to introduce the Walter parametrization scheme [10]:

$$\mathcal{H}_{\text{CF}} = W[(1-|x_1| - |x_2| - |x_3| - |x_4|)O_2^0/3 + x_1 O_2^2/2 + x_2 O_4^0/60 + x_3 O_4^2/12 + x_4 O_4^4/12].$$

(2)

The parameters $x_1$, $x_2$, $x_3$ and $x_4$ are confined to the interval $(-1, +1)$ and are chosen in such a way that $|x_1| + |x_2| + |x_3| + |x_4| \leq 1$. The parameter $W$ is a scaling factor, which can be easily deduced from the known full splitting $\Delta_2 = 425$ K of the $^2F_{5/2}$ manifold. The usual procedure to use this parametrization scheme is to prepare the computer code which allows one to move through the $(x_1, x_2, x_3, x_4)$ parameter space with small increments $\delta_i$ in each parameter ($\delta_i = 0.01$ is usually sufficient), to calculate the desired physical quantities at such a well defined mesh and to compare with the experimental results available [11]. In comparison with any available fitting procedure, this method is numerically stable and allows in general unambiguous determination of the CF parameters.

A CF of orthorhombic symmetry splits the $^2F_{5/2}$ ground-state multiplet into three Kramers doublets of $\Gamma_5$ symmetry [12]. The estimated magnetic entropy up to the 40 K is close to $R \ln 2$, confirming that the double degenerate CF ground state is well isolated on the energy scale. Furthermore, the entropy value close to $R \ln 2$ indicates a Kondo temperature $T_K$ close to or smaller than $T_N$. There are two possible magnetic-dipole transitions starting from this doublet and both of them were unambiguously identified by INS spectroscopy [4, 5].

Figure 1 displays the magnetization curves taken at 4.2 K in fields along the three principal axes [3]. For $B \parallel a$, the curve shows a change in slope at around 9 T, which can be ascribed to a metamagnetic transition connected with the destruction of the antiferromagnetic ground state. After the metamagnetic transition, the magnetization increases further and attains a value of about $1.2 \mu_B$/formula unit in the highest field of 35 T. The magnetizations measured for $B \parallel b$ and $B \parallel c$ show an almost linear increase with increasing field. Since the splitting of the CF levels at 35 T is large compared with the characteristic energy of intersite magnetic interaction estimated from the ordering temperature $T_N = 7.5$ K, we may expect to be able to reproduce the magnetization values $M_a$, $M_b$ and $M_c$ in terms of a single-ion CF scheme. Therefore, we use these values of magnetization as input to the parameter-search program.

The temperature dependence of the magnetic susceptibility measured along the three principal axes shows considerable anisotropy, which becomes more pronounced with decreasing temperature, indicating a significant influence of the CF interaction [3]. The high-temperature slopes of $\chi_i^{-1}$ against $T$ provide values of the paramagnetic Curie temperatures for each crystallographic direction: $\theta_a = -35$ K, $\theta_b = -25$ K and $\theta_c = -145$ K. On the basis of molecular-field theory [13], the values of $\theta_i$ can be related to the values of
the CF parameters $B_2^0 \simeq 11$ K and $B_4^0 \simeq 1.5$ K. We choose the crystallographic $a$ and $c$ axes as the $x$ and $z$ quantization axes, respectively. Inspecting equations (1) and (2) we find that both values of $W$ and $x_1$ should be positive. Furthermore, the crossing of the $\chi_a(T)$ and $\chi_b(T)$ dependences near 150 K, which may serve as a further test for the CF parameters, should be noted. Takabatake et al [3] analysed $\chi(T)$ using the expression $\chi^{-1}(T) = \chi_{CF}^{-1}(T) - \lambda$, where $\chi_{CF}^{-1}$ is the single-ion-based CF contribution and $\lambda$ describes the effective intersite magnetic interaction. Using this, these authors derived satisfactory agreement with $\lambda = -199 \times 10^3$ mol m$^{-3}$ and the CF parameters denoted as set I in table 1. However, this set I provides values of $M_a$, $M_b$ and $M_c$ at 35 T (table 2) which are not in agreement with experiment.

Using the CF Hamiltonian (2) and the parameter-search method, we were able to determine values of $W$, $x_1$, $x_2$, $x_3$ and $x_4$ which account for the energies and the approximate relative intensities of the two observed INS transitions, the magnetization values $M_a$, $M_b$ and $M_c$ at 35 T as well as the anisotropy of magnetic susceptibility at suitable chosen temperatures ($T = 20$, 80, 140 and 200 K in our particular case). Our numerical search proved that there is only one area of the reduced parameter space satisfying the experimental results summarized in table 2 ($W > 0$, $x_1 > 0$, $x_2 > 0$, $x_3 < 0$ and $x_4 > 0$). Having identified this area, we repeated the search in this area with the step $\delta_i = 0.005$. The best solution is represented by $W = 159$ K, $x_1 = 0.02$, $x_2 = 0.17$, $x_3 = -0.23$ and $x_4 = 0.44$ corresponding to CF parameters denoted as set II in table 1. The area of possible solutions is rather small ($0.0 < x_1 < 0.04$, $0.15 < x_2 < 0.18$, $-0.26 < x_3 < -0.22$ and $0.41 < x_4 < 0.45$), mainly because of the requirement to reproduce the magnetization data at 35 T.

Having determined the CF parameters, we compare the measured $M$-$B$ curves for the $b$ and $c$ directions with the calculated curves. The calculation of the magnetization curves has been done by means of the single-ion Hamiltonian

$$\mathcal{H} = \mathcal{H}_{CF} - gJ\mu_B B \cdot J$$

(3)
Table 1. CF parameters of CePtSn deduced from susceptibility only (set I; taken from [3]) and deduced from RS, susceptibility and high-field magnetization (set II). Also the corresponding wavefunctions are given.

<table>
<thead>
<tr>
<th>CF parameter</th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_2^0 )</td>
<td>8.5</td>
<td>7.4</td>
</tr>
<tr>
<td>( B_2^2 )</td>
<td>0.24</td>
<td>1.6</td>
</tr>
<tr>
<td>( B_4^0 )</td>
<td>-0.15</td>
<td>0.45</td>
</tr>
<tr>
<td>( B_4^2 )</td>
<td>-4.1</td>
<td>-3.05</td>
</tr>
<tr>
<td>( B_4^4 )</td>
<td>8.7</td>
<td>5.83</td>
</tr>
</tbody>
</table>

\[
\psi_0 = +0.57| \frac{1}{2} \rangle - 0.60| \frac{3}{2} \rangle + 0.56| \frac{5}{2} \rangle - 0.56| \frac{7}{2} \rangle - 0.42| \frac{1}{2} \rangle + 0.78| \frac{3}{2} \rangle - 0.47| \frac{5}{2} \rangle - 0.47| \frac{7}{2} \rangle
\]

\[
\psi_1 = -0.82| \frac{1}{2} \rangle - 0.49| \frac{3}{2} \rangle + 0.31| \frac{5}{2} \rangle - 0.31| \frac{7}{2} \rangle + 0.88| \frac{1}{2} \rangle + 0.47| \frac{3}{2} \rangle - 0.02| \frac{5}{2} \rangle - 0.02| \frac{7}{2} \rangle
\]

\[
\psi_2 = +0.09| \frac{1}{2} \rangle - 0.63| \frac{3}{2} \rangle - 0.77| \frac{5}{2} \rangle - 0.77| \frac{7}{2} \rangle - 0.21| \frac{1}{2} \rangle + 0.42| \frac{3}{2} \rangle + 0.88| \frac{5}{2} \rangle + 0.88| \frac{7}{2} \rangle
\]

where \( g_J \) is the Landé factor and \( J \) the total angular momentum. The magnetic field \( B \) contains contributions from the applied field and the dipolar and exchange interactions of the Ce\({}^{3+}\) ion with its neighbours in the mean-field approximation [14]. The latter contributions should be small in the present case but can be dominant in systems like RFe\(_2\) for example [15]. The Hamiltonian (3) yields the following expression for the magnetization:

\[
M = g_J \mu_B \sum_i \langle \eta_i | J | \eta_i \rangle \frac{\exp(-e_i/k_B T)}{Z}
\]  

(4)

where \( \eta_i \) and \( e_i \) are the \( i \)th eigenvector and eigenvalue, respectively, of the Hamiltonian (3) and \( Z \) is the partition function. We found satisfactory agreement with the experimental data for the \( b \) and \( c \) directions (see figure 1), which is improved compared with the results obtained with set I of CF parameters. In our calculations this originates from the dominant weights of the \( |\pm\frac{3}{2}\rangle \) states in the ground-state wavefunction \( \psi_0 \) (see table 1). The influence of the exchange and dipolar interaction on the calculated curves can be estimated by introducing the molecular-field parameter \( \lambda \) found by Takabatake \textit{et al} [3]. It was found that the calculated values of magnetization at 35 T changed by less than 5% (see table 2). This result encouraged us to calculate the high-field magnetization curves in the paramagnetic range \((T = 18 \text{ and } 30 \text{ K})\) and we find a rather strong curvature for the \( a \) direction (figure 2).
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Figure 2. Calculated field dependence of the magnetization of CePtSn for the three principal directions at 18 K (---) and 30 K (-----) using CF-parameter set II.

Figure 3. Calculated temperature dependence of the magnetic susceptibility of CePtSn along the three principal directions using the CF-parameter set I (-----, taken from [3]), and set II (---). The symbols denote the particular crystallographic directions.

It would be of interest to measure the high-field magnetization in the paramagnetic range in order to test our CF parameter set II further.

Furthermore, we compared the calculated temperature dependence of the magnetic susceptibility of our set II with that obtained by set I [3] (figure 3). The characteristic features of the susceptibility of CePtSn ($\chi_a > \chi_b > \chi_c$ at low temperatures, and the crossing of $\chi_a(T)$ and $\chi_b(T)$ at about 150 K) are well reproduced also by set II, although absolute agreement with the experimental data is less good than for set I.
3. Discussion and conclusions

The main purpose of this work was to determine a consistent set of CF parameters for the intermetallic compound CePtSn. We have shown that a full analysis of the experimental data (NS, magnetization and susceptibility) leads to a CF Hamiltonian reproducing these data in a satisfactory way. In [3], only the susceptibility data are taken into account, but there are at least two arguments to suggest that more attention is paid to the high-field magnetization data. First, we may assume that, as in other CeTX compounds, the coherence effects as well as the exchange interaction mainly influence the low-field \( B < 20 \) T magnetization data. In this context we can understand why, for the \( a \) axis, only the high-field parts of the experimental and theoretical magnetization curves (as shown in figure 1) approach reasonable agreement. Secondly, the ground-state CF doublet of the Ce\(^{3+}\) ion in CePrSn is split by \( \Delta_a = 59.4 \) K, \( \Delta_b = 14.8 \) K and \( \Delta_c = 10.3 \) K upon application of a magnetic field of 35 T in the \( a, b \) and \( c \) directions, respectively. These splittings exceed \( T_N \) and \( T_K \approx 10 \) K [3], which can be taken as measures of the exchange and coherence effects, respectively. Therefore the use of the single-ion Hamiltonian (3) can be justified for these high fields as well as for \( T \gg T_N, T_K \). This is supported by a recent successful analysis of the more complex intermetallic compound CeCuZSi where it was shown that a simple CF model is adequate to describe most of the observed features at temperatures well above the Kondo temperature, which is about 10 K in this compound [16].

Acknowledgments

This work was financially supported by Stichting voor Fundamenteel Onderzoek der Materie', the Charles University Grant Agency (Project 288) and the Grant Agency of the Czech Republic (Project 202/93/0184).

References