Crystal-field interactions in PrRu$_2$Si$_2$

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Abstract. We have attributed the magnetism of PrRu$_2$Si$_2$ to the Pr ions and performed calculations of the fine electronic structure of the Pr^{3+} ion in tetragonal symmetry taking into account the crystal-field and inter-site, spin-dependent exchange interactions. The energy level scheme derived is associated with the removal of the degeneracy of the lowest multiplet given by Hund's rules, ^{3}H$_4$. Magnetic and electronic properties resulting from this fine structure are compared with all known experimental results. Our calculations reproduce the zero-temperature moment, the temperature dependence of the magnetic susceptibility, the single-crystalline magnetization curves with the anisotropy field of 400 T, the specific heat with the sharp peak at T_C as well as inelastic neutron scattering data.

1. Introduction

The ternary compounds RM$_2$X$_2$ (R = rare earth; M = 3d, 4d or 5d transition metal; and X = Si or Ge) exhibit strongly anisotropic magnetic properties. PrRu$_2$Si$_2$ exhibits the largest measured value of the magnetocrystalline anisotropy. The anisotropy field at 4.2 K is estimated to be as enormous as 400 T [1]. PrRu$_2$Si$_2$ crystallizes in the tetragonal structure of ThCr$_2$Si$_2$ type and orders ferromagnetically below $T_C = 14$ K [2]. Its magnetic susceptibility displays strongly anisotropic behaviour at temperatures above T_C [3]. The temperature dependence of the specific heat of PrRu$_2$Si$_2$ shows a well-defined anomaly at the ferromagnetic ordering temperature. The temperature dependence of the magnetic entropy computed from the magnetic contribution reaches the value of $R \ln 2$ at about 30 K. It indicates the existence of two closely lying levels. Inelastic neutron scattering experiments [1,4] reveal local excitations with energies of 2.25 and 29 meV, providing a strong argument for the existence of localized CEF-like levels. The authors of reference [1] have proposed a preliminary energy level scheme making use of the observed excitations and have established the CEF ground state Γ_{t1}. This singlet ground state is also confirmed by our studies.

The aim of this paper is to evaluate, on the basis of all known experimental results, the energy level scheme of the fine electronic structure of the Pr^{3+} ion in PrRu$_2$Si$_2$ associated with the configuration 4f^2. The structure constructed provides a remarkably consistent description of the main magnetic and electronic properties of the compound under study. We have taken into account the inter-site magnetic interactions that produce the long-range magnetic order at low temperatures despite the singlet ground state.

2. Outline of the theory

In the individualized-electron model, f electrons keep their individuality even when placed into intermetallic compounds. In the intermetallic compound there coexist a few (here only

two are specified) physically important electronic subsystems: f-electronic subsystem(s) and the conduction electron subsystem. These two subsystems are described by completely different theoretical approaches: localized-electron and itinerant-electron models. The f-electron subsystem exhibits the discrete energy spectrum associated with bound states of the electronic system f^n. Itinerant electrons occupy the conduction band states. We attribute the magnetic properties of $PrRu_2Si_2$ mainly to the $4f^2$ electronic system of the Pr^{3+} ions because the conduction electron susceptibility is small and largely temperature independent, as we know from studies of $LaRu_2Si_2$ [5]. The Hund's-rules ground multiplet is $^3H_4$ with $J = 4$, $S = 1$, $L = 5$ and the Landé factor $g_L = 4/5$. The general Hamiltonian contains single-ion-like and inter-site terms [6,7]:

$$H = \sum \sum B_n^m \hat{O}_n^m(J, J_z) + n g_L^2 \mu_B^2 \left(-J\langle J \rangle + \frac{1}{2}\langle J \rangle^2 \right) + g_L \mu_B J B_{ext}. \quad (1)$$

The first term is the CEF Hamiltonian written out for the lowest multiplet given by Hund's rules, $^3H_4$. The second term represents the exchange interactions between the Pr ions given in the mean-field approximation with the molecular-field coefficient n. The third one describes the Zeeman effect.

3. Results and discussion

The energy level scheme for the Pr ion in $PrRu_2Si_2$ for the tetragonal-symmetry CEF Hamiltonian contains five singlets and two doublets [6]. A full set of CEF parameters relevant to the tetragonal symmetry is given by: $B_2^0 = -22$ K, $B_4^0 = +0.22$ K, $B_4^4 = +0.20$ K, $B_6^0 = -12$ mK and $B_6^4 = -45$ mK. This set of parameters has been derived from our self-consistent analysis of experimental data. This set of CEF parameters provides an adequate description of:

  (i) the energy separations revealed by the inelastic neutron scattering,
 (ii) the anisotropic temperature dependence of the susceptibility in the paramagnetic region,
(iii) the direction of the magnetic moment (along the tetragonal c-axis) in the ordered state,
(iv) the spontaneous moment of the Pr ion at 4.5 K of about 2.7 μ_B,
 (v) the giant magnetocrystalline anisotropy of the magnetization curves at 4.5 K,
(vi) the temperature dependence of the specific heat with the λ-type peak at T_C.

The consistent description of so many physical properties provides strong support for our theoretical approach.

The ground state is a singlet of the form

$$\Gamma_{t1}^{(1)} = 0.703|{+4}\rangle + 0.109|0\rangle + 0.703|{-4}\rangle. \quad (2)$$

The resulting energy level scheme is shown in figure 1. It provides excitations observable in inelastic neutron scattering (INS) experiments at energies of 30 K ($\Gamma_{t1}^{(1)} \rightarrow \Gamma_{t2}$) and of 330 K ($\Gamma_{t2} \rightarrow \Gamma_{t5}^{(1)}$ and $\Gamma_{t3} \rightarrow \Gamma_{t5}^{(1)}$, Γ_{t4}). These excitations have indeed been observed, in INS experiments by Mulders *et al* [1,4] (2.25 and 29 meV). In those experiments the 330 K excitation decreases with increasing temperature. We take this as further confirmation of our scheme. With the increasing temperature, the $\Gamma_{t3} \rightarrow \Gamma_{t4}$ contribution, having the lower energy, increases together with the Boltzmann population of the Γ_{t3} state. This observation provides an indirect argument for the existence of the state $\Gamma_{t3}^{(1)}$ at 58 K—neutron excitations to the Γ_{t3} state from the lower states are prohibited. As will be shown later, the existence of a state at about 60 K is in very good agreement with the overall temperature dependence of the specific
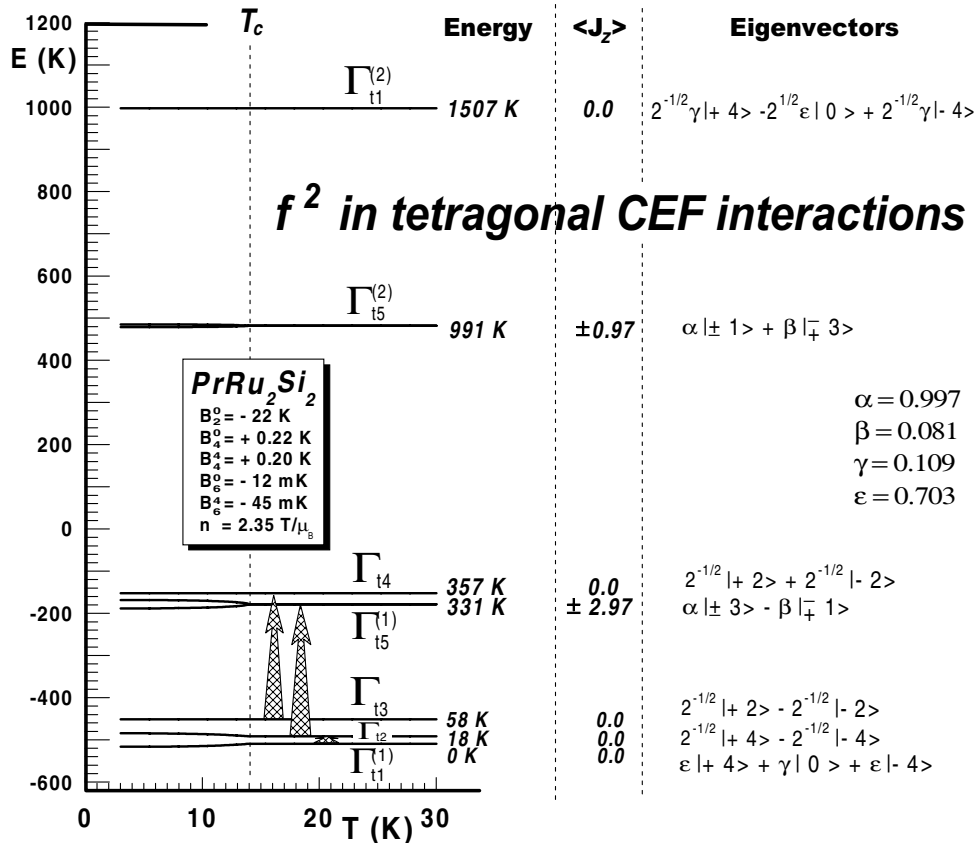
Figure 1. The energy level scheme of the Pr^{3+} ion in $PrRu_2Si_2$ with the expectation values of J_z and eigenvectors in the paramagnetic state. The tetragonal CEF interactions split the ninefold-degenerate ground multiplet $^3H_4$ into five singlets and two doublets. Three arrows indicate the allowed INS excitations. They are assigned to those experimentally detected in references [1] and [4].

heat. The entropy analysis performed in reference [1] shows that there is a place for this extra state, as the entropy calculated for two states only is too small; see figure 2 of reference [1].

The closely lying first excited state and ground state create an interesting system. Their field-induced J_z-components have opposite signs which lead to their opposite interactions with the magnetic field. As a consequence, this two-level system behaves as a quasi-doublet. Moreover, there is a large matrix element connecting these states. Thanks to this, magnetism can be relatively easily induced in this system by spin-dependent interactions, despite the general non-magnetic character of the singlets. Such a charge-formed ground state allows the appearance of a large magnetic moment, of 2.7 μ_B, in agreement with experimental observation. Also, the direction of the moment is related to the shape of the eigenfunctions of this two-level system.

3.1. Magnetic susceptibility

In the quantum paramagnetic theory, the magnetic moment is a property of the electronic state of the paramagnetic ion. The value of the magnetic moment of the ion reflects the dependence

of the energy of the ion on the magnetic field B according to the definition [8]

$$m(T) = -\frac{\delta E(T)}{\delta B}. \tag{3}$$

$E(T)$ is the total energy of the system calculated over the available electronic states resulting from the Hamiltonian (1) and shown in figure 1. The population of states shown in figure 1 is given by the Boltzmann statistics. The magnetic susceptibility in the paramagnetic region was calculated by direct diagonalization of the Hamiltonian, equation (1), without the second term.

The inverse of the calculated temperature dependence of the magnetic susceptibility in the paramagnetic region is shown in figure 2. It exhibits very anisotropic behaviour with an easy c-axis. The behaviour $\chi^{-1}(T)$ in a magnetic field parallel to the c-axis almost follows the Curie–Weiss law. The derived effective paramagnetic moment at room temperature amounts to 4.18 μ_B. It is larger than the free-ion value of 3.58 μ_B and this is caused by strong CEF interactions. This paramagnetic moment decreases with the increase of temperature, approaching the theoretical value at temperatures comparable with the overall energy of the CEF interactions. In a perpendicular field the calculated susceptibility is very small. The visible discrepancy between the calculated and experimental curves we attribute to its small value, which becomes comparable to the conduction electron contribution.
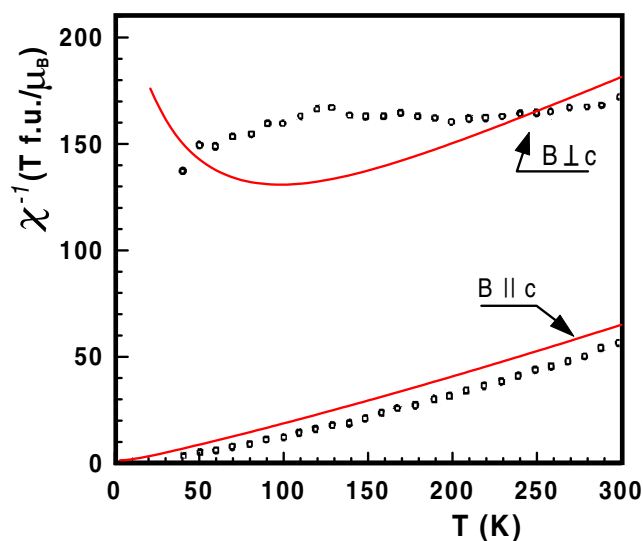

Figure 2. The temperature dependence of the magnetic susceptibility of PrRu$_2$Si$_2$ along the tetragonal c- and a-axes, shown in a χ^{-1}-versus-T plot for the paramagnetic state. The solid lines show our calculations; points are experimental data after reference [3].

3.2. The magnetic state and magnetocrystalline anisotropy

At a T_C of 14 K, the magnetic order prevails over the temperature disordering. This is accounted for in our calculations with the effective exchange interaction parameter n of 2.35 T/μ_B. The magnetic ordering produces the abrupt change in the energy level scheme that manifests itself in the λ-peak at T_C. The calculated moment of the Pr ion is parallel to the c-axis, in agreement with experiment. It amounts to 2.7 μ_B at 0 K, fully reproducing the experimental datum [1]. For completeness, we add that it turns out from our calculations that at 0 K the Pr^{3+} ion in

PrRu$_2$Si$_2$ experiences an internal molecular field of 6.4 T that originates from the inter-site RKKY interactions.

The magnetic moment of the Pr^{3+} ion is strongly tied to the tetragonal *c*-axis as we see from the magnetization curves. In figure 3 the full magnetization curves, at 4.5 K, calculated within our CEF approach are presented. They are highly anisotropic: a field of 5.5 T applied along the *c*-axis induces a $\langle J_z \rangle$ of 3.6, which is about 100 times the value of $\langle J_x \rangle$. This anisotropy is preserved also in measurements up to 35 T, where the magnetization is 3.08 μ_B and 0.39 μ_B along the *c*-axis and *a*-axis, respectively [1]. This large anisotropy is in agreement with single-crystal magnetic measurements of Shigeoka *et al* [3]. The anisotropy field derived from our calculated curves amounts to 400 T. This value corresponds to the magnetocrystalline anisotropy energy of 59 J cm^{-3}, which is extremely large.
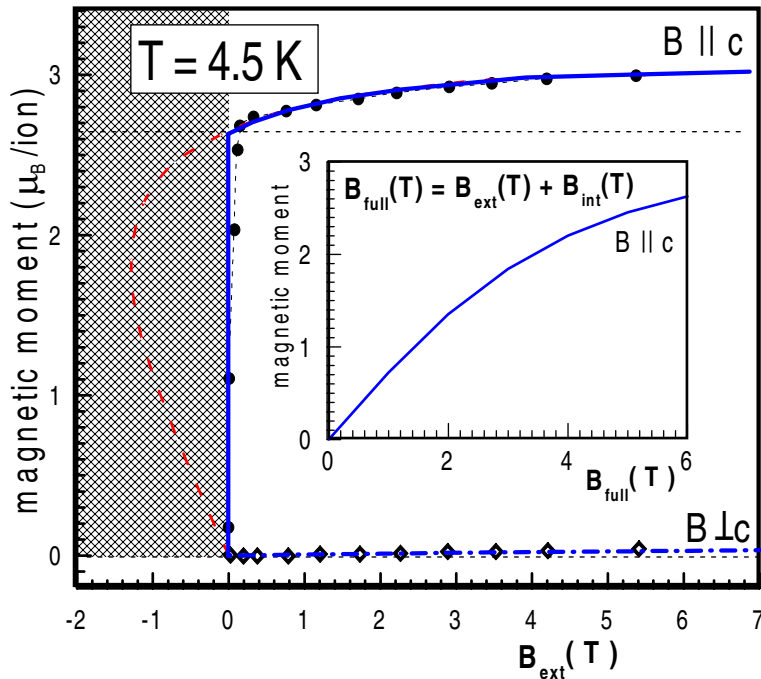

Figure 3. Magnetization curves: the moment versus the external field B_{ext}, at 4.5 K (lines) for single-crystalline PrRu$_2$Si$_2$ calculated along the main crystallographic directions of the tetragonal unit cell for the ferromagnetic state. Points denote experimental data from reference [1]. In the inset the primary field-induced magnetic moment is shown. For the ferromagnetic state, in order to take into account the influence of the external field, the internal field $B_{int} = nm$ is subtracted.

For the calculations of the magnetization curves for the ferromagnetic state along the *c*-direction, shown in figure 3, the primary field-induced moment curve $m(B_{full})$, shown in the inset, has been used. To ascertain the influence of the external field B_{ext}, the internal field $B_{int} = nm$ has to be subtracted, which leads to a metastable region at zero field. Such a metastable situation indicates the spontaneous formation of a ferromagnetic state.

The derived CEF parameters account also for the ferromagnetic ordering, including its direction, the ordering temperature and the size of the Pr-ion moment and the giant magnetic anisotropy. These calculations reveal that the giant anisotropy, even above 400 T, can be realized by the crystal-field interactions.

3.3. Specific heat

The magnetic component of rare-earth specific heat is calculated by making use of the general formula [7]

$$c_{4f}(T) = -T \frac{\delta^2 F(T)}{\delta T^2}. \tag{4}$$

$F(T)$ denotes the free energy of the rare-earth subsystem calculated over the available energy states resulting from the consideration of the Hamiltonian (equation (1)). The calculated contribution of the Pr^{3+} ions to the specific heat of $PrRu_2Si_2$ is shown in figure 4. The overall behaviour $c_{4f}(T)$ is in very good agreement with the experimentally derived magnetic contribution to the specific heat [1]. Our calculations reproduce:

(i) a λ-type peak at 14 K associated with the occurrence of the ferromagnetic order; there is a slight discrepancy as regards the description of the shape of the peak: the calculated one is wider than the experimental one—this may indicate a more dramatic character of the phase transition at T_C;
(ii) a tail of the Schottky-like peak above T_C.

The reproduction of the λ-peak is an important result from the present paper. The earlier calculations of reference [1] could not give the λ-peak because they were worked out with thermally independent electronic states. In fact, the model of reference [1] could not produce the ferromagnetic order.
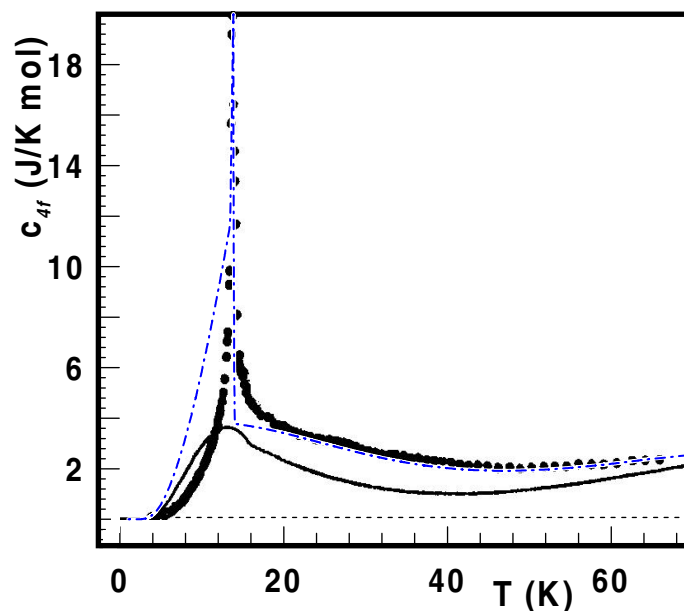

Figure 4. The temperature dependence of the 4f specific heat contribution in $PrRu_2Si_2$. The chain line shows the result of our calculations. The solid line represents the calculations of reference [1]. Points are experimental data from reference [1].

This good agreement indicates that one can have considerable confidence in the fine-electronic structure derived here. Our scheme gives a much better description of the overall $c_{4f}(T)$ dependence than previous calculations presented in reference [1]. The authors of [1]

worked with a temperature-independent structure of states, did not take into account the inter-site spin–spin interactions and were not able to reproduce the λ-peak at T_C.

4. Conclusions

The energy level scheme of the Pr^{3+} ion in PrRu$_2$Si$_2$ has been constructed on the basis of all known experimental data. Our scheme is in agreement with the inelastic neutron scattering data. Our calculations reproduce the zero-temperature moment and its temperature dependence, the temperature dependence of the magnetic susceptibility and the specific heat with the sharp peak at T_C, and also single-crystalline magnetization curves with the enormous anisotropy field of 400 T. The consistent description obtained indicates that one can have considerable confidence in the present evaluation of the crystal-field interactions in PrRu$_2$Si$_2$; it should prove a good starting point for CEF analysis of other members of the RERu$_2$Si$_2$ class of compounds.

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