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

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Abstract

Ferromagnetic compound PrRu$_2$Si$_2$ exhibits a giant magnetocrystalline anisotropy of about 400 T. Its ordered moment below $T_c=14$K reaches 2.7 $\mu_B$ and is parallel to [0 0 1] crystalline direction. 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 ion in the tetragonal symmetry, relevant to PrRu$_2$Si$_2$ taking into account crystal-field and inter-site, spin-dependent exchange interactions. Spin-dependent interactions have been taken into account by means of molecular-field approximation. The derived energy level scheme is associated with the removal of the degeneracy of the lowest multiplet given by Hund’s rules, $^3\text{H}_4$. Magnetic and electronic properties resulting from this fine structure are compared with all known experimental results. Our calculations reproduce well the zero-temperature moment, temperature dependence of the magnetic susceptibility, single-crystalline magnetization curves with the anisotropy field of 400T, the specific heat with the sharp peak at $T_c$ as well as inelastic-neutron-scattering data.

1 Introduction

Ternary compounds RM$_2$X$_2$ (R= rare earth M= 3d, 4d or 5d transition metal and X=Si or Ge) exhibit large anisotropic magnetic properties. PrRu$_2$Si$_2$ exhibits the largest measured magnetocrystalline anisotropy. The anisotropy field at 4.2 K is estimated to be so enormous as 400 T \cite{1}. PrRu$_2$Si$_2$ crystallizes in the tetragonal structure ThCr$_2$Si$_2$-type and orders ferromagnetically below $T_C=14$K \cite{2}. Its magnetic susceptibility shows strongly anisotropic behavior in temperatures above $T_C$ \cite{3}. The temperature dependence of the specific heat of PrRu$_2$Si$_2$ shows the well-defined anomaly at the ferromagnetic ordering temperature. The temperature dependence of the magnetic entropy computed from the magnetic
contribution shows value Rln2 at about 30K, indicating 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 strong argument for the existence of the localized CEF-like levels.

The aim of this paper is the evaluation, on basis of all known experimental results, of the energy level scheme of the fine electronic structure of the Pr\(^{3+}\) ion in PrRu\(_2\)Si\(_2\) associated with the configuration \(4f^2\). This structure provides consistent description of main magnetic and electronic properties of the compound under study, the direction and the ordered moment value as well as the sharp peak at \(T_C\) in the temperature dependence of the heat capacity, in particular.

2 Outline of theory

In the individualized-electron model \(f\) electrons keep their individuality also being placed into intermetallic compounds. In the intermetallic compound there coexists a few (here only 2 are specified) physically important electronic subsystems: \(f\) electronic subsystem(s) and conduction-electron (c-e) 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 have attributed the magnetic properties of PrRu\(_2\)Si\(_2\) to be predominantly due to the \(4f^2\) electronic system of the Pr\(^{3+}\) ions because the c-e susceptibility is small and largely temperature independent as we know from the studies of LaRu\(_2\)Si\(_2\) [5]. The Hund’s rules ground multiplet is \(3\text{H}_4\) with \(J = 4\), \(S = 1\), \(L = 5\) and the Landé factor \(g_L = 4/5\). The general Hamiltonian contains the single-ion-like and the intersite terms [6, 7]:

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

The first term is the CEF Hamiltonian written for the lowest multiplet given by Hund’s rules \(3\text{H}_4\). The second term represents the exchange interactions between the Pr ions written 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 of the Pr ion in PrRu\(_2\)Si\(_2\) for the tetragonal symmetry CEF Hamiltonian contains 5 singlets and 2 doublets [3]. 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, \(B_4^1 = +0.20\) K, \(B_6^0 = -12\) mK and \(B_6^4 = -45\) mK. This set of parameters
has been derived by our self-consistent analysis of experimental data. This set of CEF parameters describes well

i) the energy separations revealed by the inelastic neutron scattering,

ii) 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 in 4.5 K of about 2.7 $\mu_B$,

v) the giant magnetocrystalline anisotropy of the magnetization curves at 4.5 K,

vi) temperature dependence of the specific heat with the $\lambda-$type peak at $T_C$.

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

The ground state is a singlet in the form:

$$\Gamma_{t_5}^{(1)} = 0.703 |+4\rangle + 0.109 |0\rangle + 0.703 |−4\rangle.$$ \hspace{1cm} (2)

The resulting energy-level scheme is shown in fig.1. It provides excitations observable in inelastic-neutron-scattering (INS) experiments at energies of 30 K ($\Gamma_{t_1}^{(1)} \rightarrow \Gamma_{t_2}$) and 330 K ($\Gamma_{t_2} \rightarrow \Gamma_{t_5}^{(1)}$ and $\Gamma_{t_3} \rightarrow \Gamma_{t_5}^{(1)}, \Gamma_{t_4}$). These excitations have been observed, indeed, in INS experiments by Mulders et al. \cite{1, 2} (2.25 and 29 meV). In this experiment the 330 K excitation decreases with the increasing temperature. This fact we take as the further confirmation of our scheme. With the increasing temperature the contribution $\Gamma_{t_3} \rightarrow \Gamma_{t_4}$, having the lower energy, increases together with the Boltzmann population of the $\Gamma_{t_3}$ state. This observation provides indirect argument for the existence of the state $\Gamma_{t_3}^{(1)}$ at 58 K. the neutron excitations to it 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 heat. The entropy analysis performed in Ref. 1 shows that there is a place for this extra state owing to the increasing difference between the experimental and calculated, for two states only, entropy as one can see in Fig. 2 of Ref.1.

Closely lying first excited state together with the ground state creates the interesting system. Their field-induced $J_z$ components have opposite signs what lead to their opposite interactions with the magnetic field. As a consequence this 2-levels system behaves as the quasi doublet. Moreover, there is the large matrix element between these states. Thanks it the magnetism of this system can be relatively easily induced by spin-dependent interactions despite of general non-magnetic character of singlets. Such the charge-formed ground state allows the appearance of the large magnetic moment, of 2.7 $\mu_B$, in agreement with experimental observation. Also the direction of the moment is related with the shape of the eigenfunctions of this 2-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 dependence of the energy of the ion with respect to the magnetic field $B$ according to the definition:

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

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

The inverse of calculated temperature dependence of the magnetic susceptibility in the paramagnetic region is shown in Fig. 2. It exhibits very anisotropic behavior with the easy $c$ axis. The behavior $\chi^{-1}(T)$ in the magnetic field parallel to the $c$ axis almost follow the Curie-Weiss law. The derived effective paramagnetic moment at room temperature amounts to 4.18 $\mu_B$. It is larger than the free-ion value of 3.58 $\mu_B$ and this fact 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 size of the CEF interactions. In the perpendicular field the calculated susceptibility is very small. The visible discrepancy between calculated and experimental curves we attribute to its small value that becomes comparable to the conduction-electron contribution.

3.2 Magnetic state and magnetocrystalline anisotropy

At $T_c$ of 14 K magnetic order wins the temperature disordering. It is accounted for in our calculations with the effective exchange interaction parameter $n$ of 2.35 $T/\mu_B$. The magnetic ordering produces the abrupt change in the energy level scheme that manifests in the $\lambda$ 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 $\mu_B$ at 0 K fully reproducing the experimental datum. 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 the internal molecular field of 6.4 T that originates from the intersite 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 Fig. 3 the full magnetization curves, at 4.5 K, calculated within our CEF approach are presented. They are highly anisotropic: the field of 5.5 T applied along the $c$-axis induces $\langle J_z \rangle$ of 3.6 what is about 100 times more then the value for $\langle J_x \rangle$. This anisotropy preserves also
in measurements up to 35 T, where magnetization along the c and a axes is 3.08 \( \mu_B \) and 0.39 \( \mu_B \), respectively. This large anisotropy is in agreement with single-crystal magnetic measurements of Shigeoka et al. The anisotropy field derived from our calculated curves amounts to 400 T. This value corresponds to the magnetocrystalline anisotropy energy of 59 J/cm\(^3\), that is extremely large.

For calculations of the magnetization curves in the ferromagnetic state along the c-direction, shown in Fig. 3, the primary field-induced moment curve \( m(B_{full}) \), shown in the insert, has been used. The extraction of the influence of the external field \( B_{ext} \), the internal field \( B_{int} = n \cdot m \) has to be subtracted what leads to the metastable region at zero field. Such the metastable situation means the spontaneous formation of the ferromagnetic state.

The derived CEF parameters account also for the ferromagnetic ordering with 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):

\[
c_{4f}(T) = -T \frac{\delta^2 F(T)}{\delta T^2}
\]  

\( F(T) \) is the free energy of the rare-earth subsystem over the available energy states resulting from the consideration of the Hamiltonian (eq. 1). The calculated contribution of the Pr\(^{3+}\) ions to the specific heat of PrRu\(_2\)Si\(_2\) is shown in fig.4. The overall behavior \( c_{4f}(T) \) is in very good agreement with experimentally derived magnetic contribution to the specific heat. Our calculations reproduce well:

i) a \( \lambda \)-type peak at 14 K associated with the occurrence of the ferromagnetic order. There is slight discrepancy in description of the shape of the peak; the calculated one is wider then the experimental one. It may indicate 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 \( \lambda \) peak is important outcome of the present paper. The previous calculations of Ref. 1 could not get the \( \lambda \) peak because they worked out with thermally independent electronic states. In fact, the model of Ref.1 could not produce the ferromagnetic order.

This good agreement indicates on the substantial confidence to the presently derived fine electronic structure. Our scheme gives much better description of the overall \( c_{4f}(T) \) dependence then previous calculations presented in Ref. 1. They worked with the temperature independent structure of states as they did not take into account the intersite spin-spin interactions and they could not get the \( \lambda \) peak at \( T_c \).
4 Conclusions

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

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Figure Captions

Fig. 1. The energy level scheme of the Pr$^{3+}$ ion in PrRu$_2$Si$_2$ with the expectation values of $J_z$ and eigenvectors in the paramagnetic state. The tetragonal CEF interactions split the 9-fold degenerate ground multiplet $^3H_4$ into 5 singlets and 2 doublets. Three arrows indicate the allowed INS excitations. They are assigned to those experimentally detected in Refs 1 and 4.
Fig. 2. Temperature dependence of the magnetic susceptibility of PrRu$_2$Si$_2$ along the tetragonal c-and a-axis shown in the $\chi^{-1}$ vs T plot in the paramagnetic state. The solid lines show our calculations, points are experimental data after Ref. 3.

Fig. 3. Magnetization curves, the moment vs external field $B_{ext}$, at 4.5 K (lines) on single-crystalline PrRu$_2$Si$_2$ calculated along main crystallographic directions of the tetragonal unit cell in the ferromagnetic state. Points denote experimental data from Ref. 1. In the insert the primary field-induced magnetic moment is shown. In the ferromagnetic state, for the extraction of the influence of the external field, the internal field $B_{int} = n \cdot m$ is subtracted.

Fig. 4. Temperature dependence of the 4f specific heat contribution in PrRu$_2$Si$_2$. The dashed-point line shows the result of our calculations. The solid line represents calculations of Ref. 1. Points are experimental data from Ref. 1.
$f^2$ in tetragonal CEF interactions

| $E$ (K) | $T_c$ | Energy | $<J_2>$ | Eigenvectors |
|---------|-------|--------|---------|-------------|
|         |       | $\Gamma_{t1}^{(2)}$ | 1507 K | 0.0 | $2^{-1/2} |0\rangle - 2^{1/2} |\gamma 4\rangle$ |
|         |       | $\Gamma_{t5}^{(2)}$ | 991 K | $\pm 0.97$ | $\alpha |1\rangle \pm \beta |3\rangle$ |
|         |       | $\Gamma_{t4}^{(1)}$ | 357 K | 0.0 | $2^{1/2} |2\rangle + 2^{1/2} |-2\rangle$ |
|         |       | $\Gamma_{t5}^{(1)}$ | 331 K | $\pm 2.97$ | $\alpha |3\rangle \pm \beta |1\rangle$ |
|         |       | $\Gamma_{t3}^{(1)}$ | 58 K | 0.0 | $2^{1/2} |2\rangle + 2^{1/2} |-2\rangle$ |
|         |       | $\Gamma_{t2}^{(1)}$ | 18 K | 0.0 | $2^{1/2} |4\rangle - 2^{1/2} |4\rangle$ |
|         |       | $\Gamma_{t1}^{(1)}$ | 0 K | 0.0 | $\varepsilon |4\rangle + \gamma |0\rangle + \varepsilon |4\rangle$ |

$B_3^\pm = -22$ K
$B_3^\mp = +0.22$ K
$B_4^\pm = +0.20$ K
$B_4^\mp = -12$ mK
$B_5^\pm = -45$ mK
$n = 2.35 T_{H\parallel}$

$\alpha = 0.997$
$\beta = 0.081$
$\gamma = 0.109$
$\varepsilon = 0.703$
$\chi^{-1}(T \text{ f.u./}\mu_B)$

$PrRu_2Si_2$

$B_2^0 = -22 \text{ K}$
$B_4^0 = 220 \text{ mK}$
$B_4^4 = 200 \text{ mK}$
$B_6^0 = -12 \text{ mK}$
$B_6^4 = -45 \text{ mK}$

$B \perp c$

$B \parallel c$
$T = 4.5 \text{ K}$

$B_{\text{full}}(T) = B_{\text{ext}}(T) + B_{\text{int}}(T)$
$c_{4f} \text{ (J/K mol)}$

$Pru_2Si_2$

$B_6^0 = -22 \text{ K}$
$B_6 = 220 \text{ mK}$
$B_6^1 = 200 \text{ mK}$
$B_6^2 = -12 \text{ mK}$
$B_6^3 = -45 \text{ mK}$
$n = 2.35 \frac{T}{\mu_B}$