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Crystal-field potentials of $PrFe_2Si_2$ and $PrFe_2Ge_2$ as deduced from inelastic neutron scattering and specific heat measurements*

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Abstract. Inelastic neutron scattering experiments and specific heat measurements have been performed on polycrystalline samples of $PrFe_2X_2$ (X = Si, Ge), a tetragonal intermetallic system showing a low-temperature antiferromagnetic ordering of the Pr sublattice, with no local magnetic moment on the iron site. The temperature variation of the specific heat, and the values of the magnetic entropy, indicate for both compounds a crystal-field energy level scheme characterized by two closely spaced singlets, split by about 1 meV for X = Ge and by about 2.5 meV for X = Si, with the other levels positioned above 7 meV. These conclusions are confirmed by the observation of only one excitation peak in the magnetic neutron scattering response in this energy range. In the paramagnetic phase, the inelastic peak is centred at 2.4(1) meV for X = Si and at 0.8(1) meV for X = Ge. Below T_N, the peak position shifts to 2.8(1) meV for X = Si, and to 2.7(1) meV for X = Ge. The experimental findings are explained by a crystal- and molecular-field model with two low-lying singlets, coupled by exchange in the ordered phase. The different size of the molecular field in the two compounds, with respect to the crystal-field splitting of the low-lying singlets, causes the large difference in the ordered moments of the Pr^{3+} ions (1.41 μ_B for Si and 2.75 μ_B for Ge). The asymmetric shape of the peaks in the neutron scattering function has been attributed to the presence of two branches of magnetic excitons in these crystal-field systems showing manifestly Van Vleck-induced antiferromagnetism of singlet–singlet type.

1. Introduction

The ternary rare-earth RET_2X_2 intermetallic compounds (RE = rare-earth, T = 3d, 4d or 5d transition metal and X = Si, Ge) exhibit a wide range of electronic properties from superconductivity to heavy-fermion behaviour including intermediate valency and magnetic ordering [1–3]. Most of them crystallize in the body-centred tetragonal structure of the $ThCr_2Si_2$ type (space group $I4/mmm$). It has been reported that none of these compounds

* Dedicated to Professor Robert Troć on the occasion of his 60th birthday.

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carry any magnetic moment on the T atom except for $REMn_2X_2$ compounds. They provide a good opportunity to study the origin of the crystal field (CF) potential since the RE ion is surrounded by two nearly equidistant ligand sublattices formed by ions with very different electronic properties.

In previous publications [4, 5], we reported the results of susceptibility measurements and neutron diffraction and Mössbauer spectroscopy on $PrFe_2X_2$ (X = Si, Ge). Both intermetallic compounds undergo low-temperature antiferromagnetic ordering of the Pr sublattice with an AF type II (++−−) low-temperature structure. In both cases, the c-axis is the easy direction of the Pr moment. However, in $PrFe_2Ge_2$ an additional incommensurate–commensurate transition (IC) towards a sine-wave spin structure shows up at $T_{IC} = 9$ K. The Néel temperatures are $T_N = 7.7$ and 14.2 K, for $PrFe_2Si_2$ and $PrFe_2Ge_2$, respectively. No local moment is detected on the iron site, while the experimental value μ_0 of the ordered moment of the Pr atoms is quite different in the Si (1.41 μ_B) and the Ge (2.75 μ_B) compound. A CF interpretation of these results was also given in [4–6]. A test of our model was thought to be necessary and thus inelastic neutron scattering experiments and specific heat measurements were carried out.

The results of these new experiments are discussed below in the framework of our CF model and with reference to an inelastic neutron scattering experiment conducted at the ISIS spallation neutron source of the Rutherford Appleton Laboratory (RAL) by Osborn on $PrFe_2Si_2$ [7].

2. Experiments and results

2.1. INS experiment

$PrFe_2Si_2$ and $PrFe_2Ge_2$ were prepared from commercially available high-purity elements according to the technique described in [5]. The resulting ingots were crushed to give powdered samples for the inelastic neutron scattering (INS) experiments, whereas thin solid pellets of about 1 g were used for the specific heat measurements.

INS was carried out on the DN6 time-of-flight spectrometer of the of the Centre d'Etudes Nucléaires de Grenoble (CENG). A pyrolytic graphite monochromator and a Fermi chopper mounted before the sample were used to produce a pulsed incident neutron beam with an energy of 18 meV, higher-order contaminations being suppressed by two additional choppers. The covered scattering angle ranged from 20° to 110°. About 16 g of each product were used in the measurements at $T = 3$ K and $T = 20$ K, i.e. in both the ordered and paramagnetic phases. The measured spectra, corrected for the sample holder contribution, have been normalized to the incoherent scattering of a vanadium standard, and are shown in figure 1 in the case of $PrFe_2Si_2$. The magnetic response was identified by comparison with spectra obtained in the same conditions for the isomorphous non-magnetic compound $LaFe_2Si_2$ (solid line in the inset of figure 1). Unfortunately, the presence of spurious signals above ~9 meV limited the accessible energy transfer range.

A second INS experiment was performed with improved resolution in the low-energy-transfer range by using the multichopper time-of-flight spectrometer MIBEMOL of the Laboratoire Léon Brillouin (LLB) at the Centre d'Etudes Nucléaires de Saclay (CENS), near Paris. Several values of neutron incident energies (from 1.66 to 9.1 meV) were used in order to cover the energy range of interest. The results obtained confirmed those of DN6 and allowed us to assess the low-energy part of the CF spectrum of both compounds. Figure 2 shows the spectra at $T = 2$ K and $T = 20$ K for $PrFe_2Si_2$; the corresponding spectra for $PrFe_2Ge_2$ are shown in figure 3.

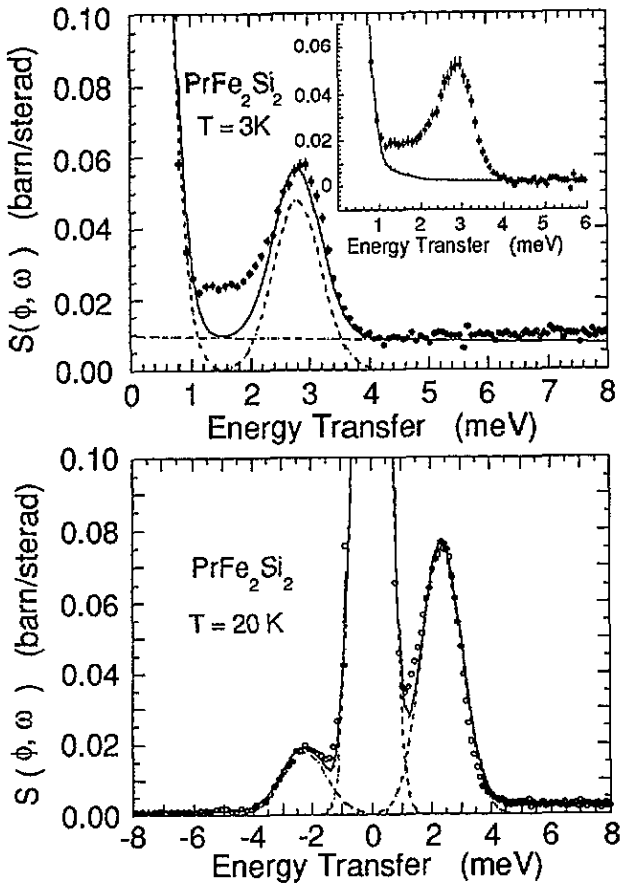

Figure 1. Neutron spectra obtained with the DN6 spectrometer in the ordered phase ($T = 3$ K) and in the paramagnetic phase ($T = 20$ K) of $PrFe_2Si_2$. The continuous line represents the result from the fitting procedure with a constant background and Gaussian lineshapes (dashed lines). At $T = 3$ K an excitation at 2.85 meV is observed, which shifts to 2.4 meV as the temperature is raised to 20 K. The inset shows the comparison with the spectrum recorded at $T = 3$ K for the isomorphous non-magnetic compound $LaFe_2Si_2$.

2.2. *Specific heat experiment*

The specific heat of $PrFe_2Si_2$ was measured by using the ac calorimetry technique, at temperatures ranging from 1.7 to about 40 K (figure 4). The details of this technique can be found elsewhere [8]. In order to subtract the lattice contribution, the specific heat of the non-magnetic isomorphous compound YFe_2Si_2 was measured too (figure 4). For the latter, fitting the low-temperature part (2–20 K) leads to an electronic contribution to the specific heat of $\gamma = 20$ mJ K^{-1} mol^{-1}, while the Debye temperature reaches $\Theta_D = 300$ K. The lattice contribution for the magnetic compounds was then deduced from the YFe_2Si_2 variation by means of a many-Debye-temperature model [8]. The resulting magnetic contributions to the specific heat, C_{mag}, are shown in figures 5 and 6 for $PrFe_2Si_2$ and $PrFe_2Ge_2$, respectively.

For $PrFe_2Si_2$, applying the model by taking into account the different molar masses of Pr and Y leads to an overestimation of the lattice contribution, resulting in a negative magnetic

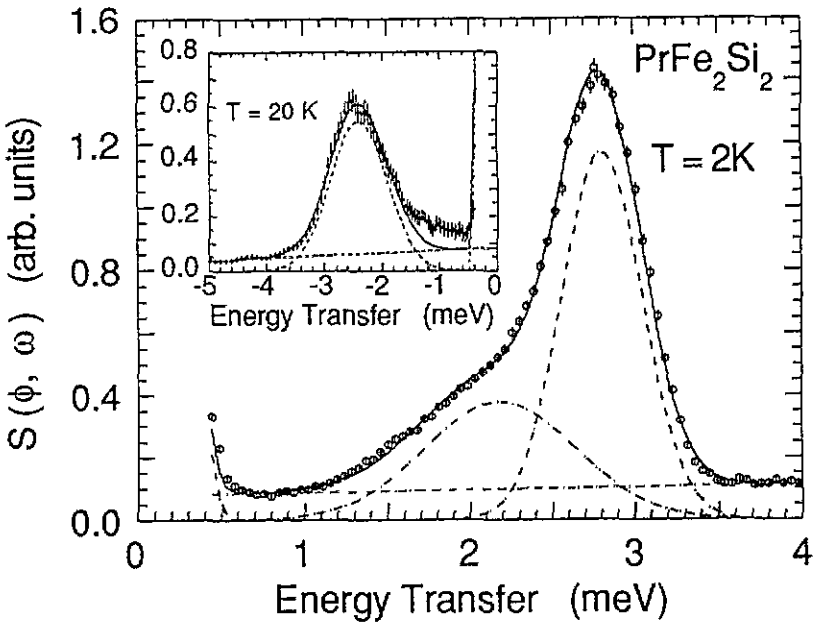

Figure 2. Neutron spectrum obtained on MIBEMOL with $E_i = 6.7$ meV in the ordered phase of $PrFe_2Si_2$ ($T = 2$ K). Phonon contributions have been subtracted by comparison with the spectrum measured for $LaFe_2Si_2$. The solid line is the fit to the data of a constant background and three Gaussians, centred at the origin, at 2.2 and at 2.8 meV, respectively (dash–dotted lines). The neutron energy gain part of the spectrum obtained at $T = 20$ K with an incident energy of 3.3 meV is shown in the inset. The peak position is at 2.4 meV.

contribution above ~30 K. Therefore, *an intermediate effective Debye temperature value* of $\Theta_D = 288$ K has been used, giving a reasonable variation for $C_{mag}(T)$ (figure 5). The occurrence of the magnetic ordering is then evidenced by a very small anomaly ($\Delta C_{mag} \sim 0.1$ J K^{-1} mol^{-1}) situated at $T_N = 7.5$ K, in good agreement with previous determinations [5]. Above T_N, a Schottky anomaly is present as a broad bump, centred around 10 K, which suggests the presence of excited CF levels lying near 25–30 K above the ground state. The magnetic entropy S_{mag} can be deduced by direct integration of C_{mag}/T (figure 5). Its value does not reach R ln(2) at 30 K, indicating that the CF levels involved at low temperature are two singlets (not doublets) well separated from the other excited levels.

For $PrFe_2Ge_2$, applying the many-Debye-temperature model leads to an effective Debye temperature value of $\Theta_D = 243$ K, giving rise to a satisfactory magnetic contribution, although YFe_2Si_2 has been taken as reference instead of YFe_2Ge_2 (figure 6). Here the Néel temperature is clearly visible as a well defined anomaly located at 14.4 K, with a jump in the specific heat of about $\Delta C_{mag} = 5.7$ J K^{-1} mol^{-1}. No anomaly is visible at 9 K. Above T_N, a magnetic contribution still subsists but no clear Schottky anomaly is visible. However, unlike for $PrFe_2Si_2$, the magnetic entropy reaches about 4.7 J K^{-1} mol^{-1} at T_N, and $S_{mag} \sim R$ ln(2) at about 23 K. It follows that only two singlets, separated by 10–15 K, are involved as low-lying CF levels below at least 80 K.

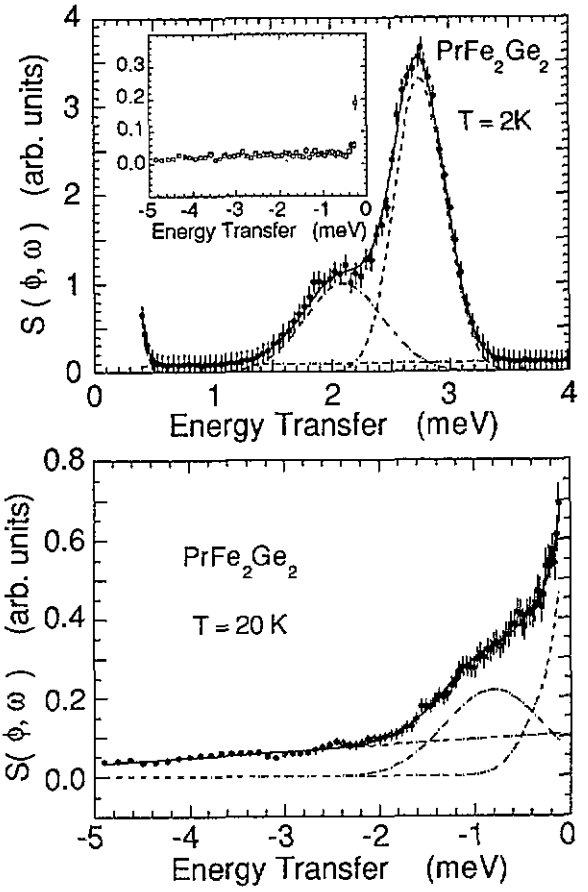

Figure 3. Neutron spectra obtained on MIBEMOL in the ordered phase ($T = 2$ K) and in the paramagnetic phase ($T = 20$ K) of $PrFe_2Ge_2$. The data at 2 K have been taken with an incident energy $E_i = 9.1$ meV, and can be fitted (solid line) by a constant background and three Gaussians centred at the origin, at 2.1 and at 2.7 meV, respectively (dash–dotted lines). The neutron energy gain part of the spectrum is shown in the inset. The data at 20 K have been collected with $E_i = 3.3$ meV. The solid line is the result of the fitting procedure with a sloping background and two Gaussians centred at the origin and at 0.8 meV, respectively (dash–dotted lines).

3. Crystal-field model

The Pr^{3+} ions correspond to the $4f^2$ electronic configuration where the $J = 4$ multiplet is the ground manifold in the Russell–Saunders coupling scheme. The corresponding free-ion moment value is 3.20 μ_B. The observed reduction of the moment value in both $PrFe_2Si_2$ and $PrFe_2Ge_2$, with a ratio 1:2 between them, made us think of crystal-field effects possibly with a singlet as ground state. This hypothesis was also confirmed by the specific heat results presented in this paper.

From a structural point of view, it would be surprising if the CF were substantially different in the Si and Ge compounds. In fact, we have shown [4, 5] that it is possible to account for the observed moment ratio with rather similar CF level schemes differing

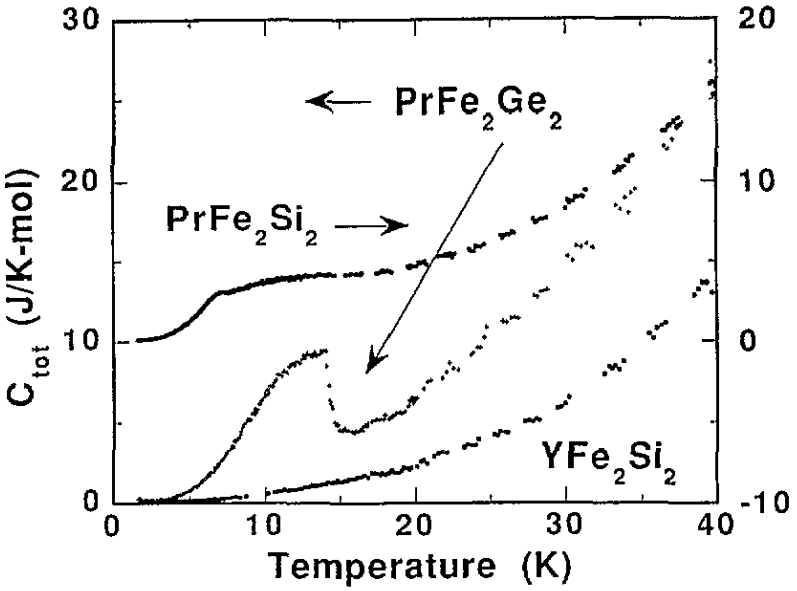

Figure 4. The total experimental specific heat of $PrFe_2Si_2$, $PrFe_2Ge_2$ and the isomorphous non-magnetic compound YFe_2Si_2 up to 40 K.

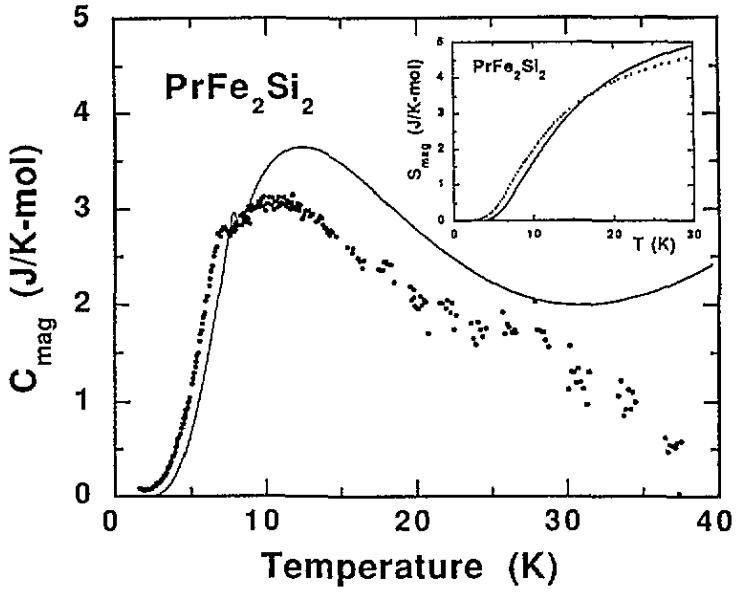

Figure 5. The magnetic contribution to the specific heat of $PrFe_2Si_2$. The continuous line represents the calculated C_{mag} starting from the CF parameters in table 2. The inset shows the magnetic entropy deduced from the experimental C_{mag} and that calculated from the model (continuous line).

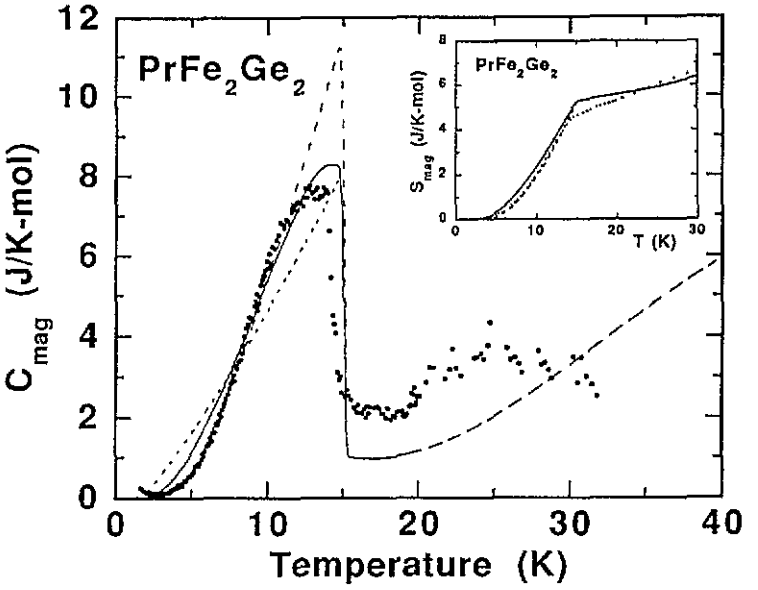

Figure 6. The magnetic contribution to the specific heat of $PrFe_2Ge_2$. The continuous line represents the calculated C_{mag} starting from the CF parameters in table 2 in the frame of the self-consistent periodic field model (see text). The dashed and the dotted lines represent the specific heat curves calculated for a simple antiferromagnet and for a magnetic structure presenting modulated character below T_N, respectively. The inset shows the magnetic entropy deduced from the experimental C_{mag} and that calculated from the periodic field model (continuous line). The calculation for a simple antiferromagnet is also shown as a dashed line, which is superimposed to the experimental curve up to T_N, where it reaches the continuous curve.

principally in the details of the low-lying part of the spectra.

In tetragonal symmetry, the total Hamiltonian for the f^2 configuration, in the presence of a molecular-field (MF) term, is

$$H = H_{CF} + H_{MF} \tag{1}$$

with

$$H_{CF} = B_2^0\hat{O}_2^0 + B_4^0\hat{O}_4^0 + B_4^4\hat{O}_4^4 + B_6^0\hat{O}_6^0 + B_6^4\hat{O}_6^4 \tag{2}$$

and

$$H_{MF} = -h\hat{J}_z. \tag{3}$$

Here

$$h = g_J\lambda\mu_B^2 N_A\mu_{ord} \tag{4}$$

where λ is the molecular-field constant, N_A the Avogadro number, $g_J = 0.8$ the Landé g-factor and $\mu_{ord} = g_J\langle\hat{J}_z\rangle$ the expectation value of the moment along z in units of Bohr magnetons.

The diagonalization of (2) in the absence of a molecular field leads to seven CF eigenstates, namely:

(i) two doublets: $\Gamma_{t5}^{(1)}$ and $\Gamma_{t5}^{(2)}$;
(ii) five singlets: $\Gamma_{t1}^{(1)}$, $\Gamma_{t1}^{(2)}$, Γ_{t2}, Γ_{t3}, Γ_{t4}.

The molecular-field term H_{MF} lifts the degeneracy of the doublets.

In [5], a calculation based on an empirical electrostatic model (the 'layer' model) developed in [9, 10], together with estimates of the second-order parameter B_2^0 based on ^{155}Gd Mössbauer data in isomorphous $GdFe_2X_2$ compounds, allowed us to propose a sequence of levels with the $\Gamma_{t1}^{(1)}$ singlet as ground state. The first excited state was thought to be the singlet Γ_{t2} in the Si and the doublet $\Gamma_{t5}^{(1)}$ in the Ge compound. The overall splitting was estimated as about 30 and 24 meV, respectively. The detailed schemes are given in [5]: the two are comparable, showing the CF levels to be divided in two groups, one at low and the other at high energy.

We have also shown in [6] that it is possible to treat the problem of the $J = 4$ multiplet in tetragonal symmetry, allowing for a ground state of the $\Gamma_{t1}^{(1)}$ type, by introducing an alternative parametrization of the CF Hamiltonian (2) where the various parameters have a more intuitive physical meaning than the usual crystal-field parameters (CFP). In this scheme, we can easily select the sets of CFP which are solutions of the self-consistent CF + MF problem with fixed values of the ordered moment μ_{ord} and of the ordering temperature T_{ord}. This temperature is related to λ by the condition $\lambda = 1/\chi_z^{VV}(T_{ord})$, χ_z^{VV} being the z-component of the single-ion Van Vleck susceptibility. These solutions depend on the parameters $(x, B_2^0, \Delta, \Delta_0, \epsilon, \lambda)$. x is the usual Lea, Leask and Wolf (LLW) parameter [11], characterizing the cubic part of H_{CF} [6]; Δ is the splitting between Γ_{t2} and $\Gamma_{t1}^{(1)}$; Δ_0 is the energy (relative to the ground state) of the barycentre of the two singlets Γ_{t3} and Γ_{t4}; ϵ is the coefficient of the $(|4\rangle + |-4\rangle)$ component of the ground $\Gamma_{t1}^{(1)}$ singlet.

The evolution of this approach on the light of the new experimental evidence (INS and specific heat) will be discussed in 4.3.

4. Interpretation of the results and discussion

4.1. INS experiments

Both the DN6 and the MIBEMOL spectra at low temperature (figures 1, 2 and 3) show the presence of a broad inelastic peak at 2.8(1) and 2.7(1) meV for the Si- and the Ge-based compound, respectively. However, a considerable amount of magnetic scattering is also present in the intermediate region between the elastic and the inelastic peak.

At 20 K, a peak at 2.4(1) meV was found in $PrFe_2Si_2$ on both DN6 (figure 1) and MIBEMOL (figure 2). The result was less clear for $PrFe_2Ge_2$, since the DN6 spectrum showed only an asymmetric broadening of the elastic peak. For this reason, the MIBEMOL experiments at 20 K were principally addressed to resolving the possible CF transition below 1 meV in the Ge-based compound. However, at $E_i = 3.3$ meV and positive energy transfer, the presence of a spurious peak in the energy range of interest prevented us from obtaining a clear answer. In contrast, as shown in figure 3, in the neutron energy gain part of the spectrum, the presence of a broad peak at 0.8(1) meV is clearly visible. For comparison, the same region of the spectrum at 2 K is shown in the same figure. A residual quasielastic contribution is discernible at 20 K, which could be of nuclear origin, but could also be indicative of the presence of a soft mode, whose contribution should be maximum in the proximity of T_N [12].

In principle the asymmetric shape of the inelastic peaks could be related to the presence of at least two CF transitions below ~3 meV. Therefore, it was crucial to check the number and the identity of the low-lying levels by measuring the temperature variation of the specific heat and of the magnetic entropy. As will be discussed later, the presence of more than one excited singlet below 3 meV can now be excluded.

Finally, in order to obtain a realistic CF level scheme, we have to take into account that an INS spectrum of $PrFe_2Si_2$ was obtained at ISIS (UK) on HET by Osborn [7] at $T = 100$ K in the energy range 5 to 50 meV (neutron incident energy: 60 meV). A set of CFP was given in [7] accounting well for the observed spectrum.

In spite of some similarities, important differences exist between the two CF models in [7] and in [5]. We will show in the following that a set of CFP closer to our previous estimate [5] than to the set proposed in [7] can account fairly well for all the measured properties of $PrFe_2Si_2$. In the same region of parameters, a very satisfactory solution can also be found for $PrFe_2Ge_2$.

4.2. Specific heat experiment

Within the ordered phase, the specific heat temperature variation has been calculated by using, in the case of $PrFe_2Ge_2$, the self-consistent periodic field model [13], which takes explicitly into account the modulated character of the magnetic structure at T_N. The CFP are also required, as they may drastically modify the magnitude and shape of the specific heat [14]. As a main consequence of the modulation of the magnetic moments below T_N, the specific heat jump at T_N (ΔC_{mag}) is reduced by a factor of two-thirds compared to the discontinuity expected for a simple antiferromagnet. This is illustrated in figure 6, where the specific heat variations have been calculated under both assumptions, using the CFP and MF constants given in 4.3. Moreover, the shape of the specific heat curve below T_N can be strongly affected by the exchange coefficients $J(nQ)$ corresponding to the harmonics of the basic propagation vector Q of the magnetic structure. We have used the values 1.05, 0.83 and 0.90 K for $n = 1, 3, 5$, respectively. In $PrFe_2Ge_2$, the proximity of Q and of the commensurate vector $Q_{AF} = (0, 0, \frac{1}{2})$ justifies the values of the $J(3Q)$ and $J(5Q)$ coefficients chosen in our calculation, as $3Q$ and $5Q$ are close to Q itself. It is worth noticing that, in this compound, the calculation corresponding to a simple antiferromagnetism is in quite good agreement with the experimental C_{mag} variation below 9 K, as expected, due to the locking of the propagation vector onto Q_{AF} below this temperature.

In $PrFe_2Si_2$, the calculation with Q_{AF} is valid in the whole ordered phase, in agreement with the neutron diffraction results (figure 5).

4.3. Revising the CF models

Before INS and specific heat experiments were performed, we based our interpretation of the magnetic properties of $PrFe_2Si_2$ and $PrFe_2Ge_2$ on a CF + MF model [5] which was able to account self-consistently for the markedly different values of μ_0 and T_N in these compounds. From an exhaustive analysis of the CF + MF problem, we have shown in [6] that the possible solutions accounting for the experimental values of both μ_{ord} and T_{ord} can be found in a very narrow range for the parameters. The sets of CF coefficients proposed in [5] lie in this range.

The fact that the INS and heat capacity experiments, although confirming the size of the overall CF splitting and the singlet nature of the ground state, give a partly different picture of the low-lying level positions forces us to consider less restrictive constraints on μ_{ord} and T_{ord}. This could also be a consequence of the molecular-field approximation, which must be taken with care, particularly in determining the value of the critical temperature.

We have shown that it is possible to justify the new experimental results by remaining close to the region proposed by [5] in the parameter space.

This can be easily done with the method described in [15], by analysing firstly the paramagnetic phase, where it is more convenient to pass to the alternative set of parameters (ACFP: $W, x, y, \Delta_0, \epsilon$). Here W is the usual LLW scaling factor, $y = B_2^0/W$ and the other parameters have the meaning defined in section 3.

Once a satisfactory description of the high-temperature phase is obtained (particularly in the case of $PrFe_2Si_2$, where the full INS spectrum was available), the antiferromagnetic region is examined with the method described in [6], in order to check the self-consistency condition linking μ_{ord} and T_{ord} for a given CF level scheme. The final parameters are selected by searching for the best compromise between the calculated values of μ_{ord} and T_{ord} and the corresponding experimental values μ_0 and T_N.

A few feedback trials are sufficient to locate the best solutions.

Table 1. Alternative set of crystal-field parameters (ACFP) in the models discussed in the text.

	W (meV)	x	y	Δ_0 (meV)	ϵ
$PrFe_2Si_2$					
Model [7]	0.278	−0.5486	−3.45	43.7	0.686
This work	0.960	0.9838	−0.82	35.7	0.686
Model [5]	0.630	0.9925	−0.88	18.3	0.686
$PrFe_2Ge_2$					
This work	0.335	0.9800	−0.80	19.9	0.682
Model [5]	0.590	0.9878	−0.70	13.2	0.678

Table 2. The final set of CF parameters B_n^m (in meV) leading to the energy levels of the $PrFe_2X_2$ compounds in the paramagnetic phase.

	B_2^0	B_4^0	B_6^0	B_4^4	B_6^4
$PrFe_2Si_2$	−0.788	-0.399×10^{-2}	-0.486×10^{-4}	0.787×10^{-1}	-0.259×10^{-3}
$PrFe_2Ge_2$	−0.268	-0.630×10^{-2}	-0.546×10^{-5}	0.273×10^{-1}	-0.112×10^{-3}

The resulting ACFP are shown and compared with previous work in table 1 for the Si- and Ge-based compound. In table 2 the usual B_n^m parameters are given for this work (see [5] and [7] for the other cases). From the data for $PrFe_2Si_2$ in table 1 it appears that the solution proposed here belongs to the same region of the parameter space as that in [5], but is rather far from that proposed in [7].

The CF energies relative to the $\Gamma_{t1}^{(1)}$ ground state in the paramagnetic region are given in table 3 for $PrFe_2Si_2$ and for $PrFe_2Ge_2$, together with the transition probabilities relevant for the neutron spectra. A comparison with [7] is also made for the Si-based compound.

As regards the ordered region, for $PrFe_2Si_2$ it was found that μ_{ord} can become close to the experimental value only by assuming for T_{ord} a value somewhat greater than T_N. Typically, $T_{ord} = 10$ K leads to $\mu_{ord} = 1.40\ \mu_B$. This is in line with the fact that the MF approximation overestimates the transition temperature. With $T_{ord} = 7.7$ K we would obtain $\mu_{ord} = 0.94\ \mu_B$. By using the CFP given in [7], we found even smaller self-consistent values for μ_{ord} than in our case, namely 1.22 and 0.78 μ_B at $T_{ord} = 10$ K and 7 K, respectively.

Table 3. CF energies (E, in meV) relative to the $\Gamma_{t1}^{(1)}$ ground state; excitation energies (E_t, in meV) and transition probabilities (P_t) of the main transitions for: (a), $PrFe_2Si_2$ at $T = 100$ K, in comparison with the results of the model in [7]; (b), $PrFe_2Ge_2$ at $T = 20$ K. (The levels are numbered from 0 to 6 starting from the ground state $\Gamma_{t1}^{(1)}$.)

		Γ_{t2}	$\Gamma_{t5}^{(1)}$	Γ_{t4}	$\Gamma_{t1}^{(2)}$	$\Gamma_{t5}^{(2)}$	Γ_{t3}	
$PrFe_2Si_2$								
Model [7]	E	2.7	19.5	40.7	44.9	45.5	46.7	
This work	E	2.5	20.3	20.9	43.3	47.7	50.6	
Transitions		$0 \rightarrow 1$	$1 \rightarrow 2$	$0 \rightarrow 2$	$2 \rightarrow 3$	$2 \rightarrow 6$	$1 \rightarrow 4$	$0 \rightarrow 5$
Model [7]	E_t	2.7	16.8	19.5	21.2	27.2	42.2	45.5
$T = 100$ K	P_t	5.09	0.98	1.32	0.22	0.26	0.24	0.36
Transitions		$0 \rightarrow 1$	$1 \rightarrow 2$	$0 \rightarrow 2$	$2 \rightarrow 4$	$2 \rightarrow 5$	$1 \rightarrow 4$	$1 \rightarrow 5$
This work	E_t	2.5	17.8	20.3	23.0	27.4	40.8	45.2
$T = 100$ K	P_t	4.92	0.68	1.60	0.12	0.20	0.22	0.30
$PrFe_2Ge_2$								
	E	0.9	12.3	13.4	14.7	22.5	25.1	
Transitions		$0 \rightarrow 1$	$1 \rightarrow 2$	$0 \rightarrow 2$	$1 \rightarrow 3$	$1 \rightarrow 5$	$0 \rightarrow 5$	
	E_t	0.9	11.4	12.3	12.5	21.6	22.5	
$T = 20$ K	P_t	6.26	0.24	1.66	0.27	0.74	0.48	

Table 4. CF energy values (E, in meV) and transition probabilities from the ground state (P_t) at $T = 3$ K for: (a), $PrFe_2Si_2$ and (b), $PrFe_2Ge_2$. The energies are relative to the $\Gamma_{t1}^{(1)}$ ground state. The doublet states split by the molecular field are labelled by the sign of J_z in their $J_z = \pm 3$ component. The values of h, of the assumed T_{ord} and of the calculated μ_{ord} are given in the text.

		Γ_{t2}	$\Gamma_{t5+}^{(1)}$	$\Gamma_{t5-}^{(1)}$	Γ_{t4}	$\Gamma_{t1}^{(2)}$	$\Gamma_{t5+}^{(2)}$	$\Gamma_{t5-}^{(2)}$	Γ_{t3}
$PrFe_2Si_2$									
	E	2.8	20.2	20.7	21.1	43.5	47.8	47.9	50.7
	P_t	8.03	2.15	1.04	0.00	0.03	0.06	0.00	0.00
$PrFe_2Ge_2$									
	E	2.7	13.2	13.2	14.3	15.5	22.7	24.0	26.0
	P_t	1.21	1.71	0.34	0.18	0.00	1.05	0.00	0.00

In table 4, the energy levels and the transition probabilities from the ground state for $PrFe_2Si_2$ are given in the ordered phase. The value $h = 0.16$ meV has been used for the molecular field, corresponding to the values of T_{ord} and μ_{ord} quoted above. It can be seen that, due to the small value of h, the shift of the first excited singlet with respect to the ground state is quite small, leading to an energy difference of 2.8 meV in good agreement with the experimental finding.

The final energy level scheme in the paramagnetic phase is shown in figure 7.

The comparison between the observed and the calculated magnetic specific heat and entropy is shown in figure 5.

The results for $PrFe_2Ge_2$ are also shown in figure 7 in the absence of a molecular field.

With the lack of INS spectra in the high-energy range, we have a smaller number of constraints than in the previous case. However, the high value of μ_0 and the big shift of the $\Gamma_{t1}^{(1)} \rightarrow \Gamma_{t2}$ transition as an effect of the molecular field allows us to restrict considerably the range of possible solutions. The values of the B_n^m parameters given in table 2 remain of the same order and of the same sign as those of $PrFe_2Si_2$, in accordance with our previous considerations on the structural similarity of the two compounds.

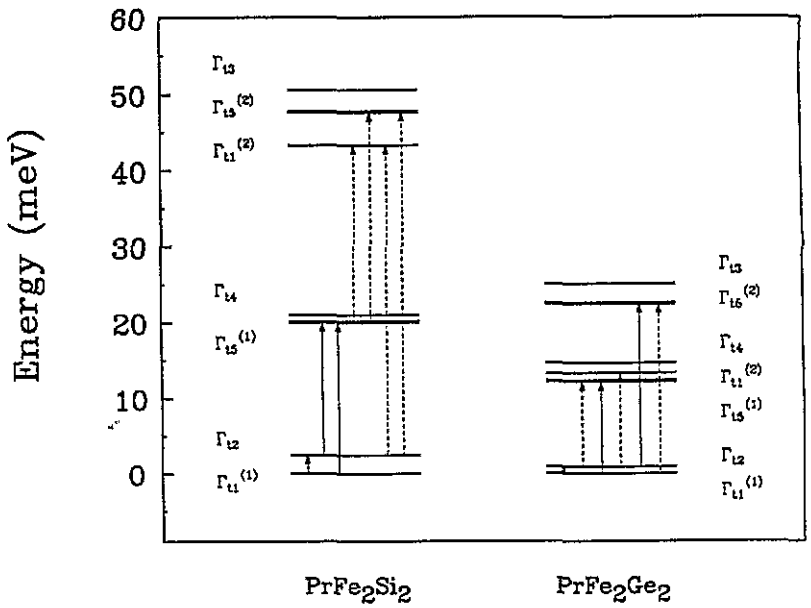

Figure 7. Energy level scheme for $PrFe_2Si_2$ and $PrFe_2Ge_2$, in the absence of a molecular field, as obtained from the CF parameters in table 2. The main transitions related to the INS spectra are also shown according to table 3.

The position of the first excited singlet is now at 0.9 meV, quite close to MIBEMOL finding. All other transitions are higher than 12 meV and the overall splitting is of the order of 25 meV, the same as in [5]. Besides, as required by INS and specific heat results, the doublet $\Gamma_{t5}^{(1)}$ and the singlet Γ_{t4} are shifted up to an intermediate range of energy around 13 meV. Obviously, this level scheme must be taken with care in the absence of further CF spectroscopy information. In particular, we have no precise control on the position of the $\Gamma_{t5}^{(1)}$ doublet, since a variation of few meV around the value quoted above does not influence in practice the calculated μ_{ord}. On the other hand, its transition probability from the ground state is quite large and this level should be observed in an INS experiment at higher energies.

In the ordered phase (see table 4), by assuming an ordering temperature $T_{ord} = 15$ K, slightly greater than T_N, the self-consistency condition is fulfilled by $\mu_{ord} = 2.91\mu_B$, not far from the neutron result of [5]: 2.75(4) μ_B. The value of molecular field, $h = 0.33$ meV, is more than twice that for the Si-based compound and is strong enough to provoke an upward shift of Γ_{t2} to 2.7 meV, in agreement with the INS experiments.

In figure 6, the magnetic specific heat and entropy calculated from the proposed CF model are displayed and compared to the experimental results.

4.4. Magnetic excitations

As anticipated, the asymmetric shape of the low-energy INS peak observed in both compounds can be related to dispersion of the CF excitations due to exchange interaction (the so called 'magnetic excitons' [12, 6, 7]). This effect has already been observed in powdered samples, as in the case of UPd_3 [18], where the various dispersion modes [19] contribute

with different weights to the shape of the inelastic peak. On the other hand, specific heat experiments preclude the presence of more than one CF transition below 3 meV, so that we are left with the previous hypothesis as the most plausible one.

To gain an idea of dispersion effects in these compounds, we can analyse our results in the light of the simplified model outlined by Fulde in [20]. We consider a two-singlet CF model, neglecting the other excited states (which is realistic in the present case), and we assume isotropic exchange, replacing the RE–conduction electron interaction by an effective RE ion–ion coupling. Since the magnetic Pr sublattice has a two-ion basis, the dispersion relations consist of two branches, acoustic and optical. INS measurements in single crystals could allow in principle a complete experimental determination of the dispersion of the magnetic excitons. The CF model could then be used to fit the dispersion curves and to obtain the q-dependence of the exchange parameters [21].

In the lack of detailed information from single-crystal INS, we limited ourselves to calculating the dispersion at the antiferromagnetic wavevector Q_{AF} in both compounds, either in the paramagnetic or in the ordered state.

The calculation of the exciton frequencies ω_{AF} gives, for $PrFe_2Si_2$, 1.3 and 1.4 meV at $T = 0$ and $T = 20$ K, respectively. For $PrFe_2Ge_2$, we obtain 2.5 and 0.4 meV at the two temperatures. The corresponding dispersions (Δ–ω_{AF}) are 1.5 and 1.1 meV for the first compound, 0.2 and 0.5 meV for the second.

If we assume that Δ–ω_{AF} gives a rough estimate of the half width at half maximum (HWHM) of the INS peaks (with the hypothesis that the dispersion effect is dominating), we see that the broadening of the peak with temperature is well reproduced in $PrFe_2Ge_2$, where the HWHM ranges from 0.15 to 0.33 meV at low temperature and is about 0.53 meV at 20 K (figure 3).

In $PrFe_2Si_2$ we would expect a width at least twice that in the Ge-based compound. However, it appears from figure 2 (HWHM $\sim$ 0.22–0.49 at $T = 0$ K and HWHM $\sim$ 0.58 at 20 K) that this is not the case, although the width remains somewhat larger than in the Ge case, particularly as regards the low-energy component of the peak. Also the trend with temperature is not respected in $PrFe_2Si_2$, but the relative variation of both Δ–ω_{AF} and of the HWHM is less important here than in the other compound, where the effect of the molecular field is very much enhanced.

Without further speculating, in the absence of a detailed knowledge of spectral distribution and intensity of the exciton modes, and from a qualitative point of view we remain of the opinion that the asymmetric shape of the magnetic peaks can be attributed to the presence of two excitonic branches, each one having an intrinsic width dominated by dispersion effects. The fact that this width is smaller for the Ge- than for the Si-based compound is in line with our calculation.

5. Conclusions

We have presented inelastic neutron spectroscopy and heat capacity data to check a previous attempt to interpret the electronic properties of the compounds $PrFe_2X_2$ by a CF + MF model. The results of these new experiments have led us to modify the parameters of the model, by retaining, however, the main physical features and assumptions of the previous interpretation.

The Pr^{3+} ion ground state multiplets, responsible for the magnetic properties, are split by CF effects. The overall energy splitting is of the order of 50 meV for the Si compound and 25 meV for the Ge one. Their CF energy scheme is essentially the same in the paramagnetic

phase. In particular, the two low-lying states are singlets, which are coupled by exchange in the ordered phase. The different size of the MF in the two compounds, relative to the CF splitting of the singlets, causes the large difference in the ordered moments of the Pr^{3+} ions.

Finally, the asymmetric shape of the INS peaks has been attributed to the presence of two branches of magnetic excitons in these crystal-field systems showing manifestly Van Vleck-induced antiferromagnetism of singlet–singlet type.

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