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Ferromagnetism and crystal electric field in the cerium compound CeRh_3B_2

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Abstract

The magnetic behavior of CeRh_3B_2 is very unusual: it orders ferromagnetically with an exceptionally high Curie temperature T_C around 115 K, but with a small saturation moment of about $0.4 \mu_B/\text{fu}$. The thermal variations of magnetization and susceptibility have been measured on a single crystal for fields applied along the easy and hard magnetization directions, with, in the latter case, special care taken to avoid rotation of the sample. The results are compared to calculations based on the crystalline electric field formalism. Due to its large value, one has to take into account the admixture of the two J multiplets of the Ce^{3+} ion as it is usually used for samarium compounds but not for cerium ones. These calculations actually show the important role of the excited $J' = 7/2$ multiplet on the $4f$ spin moment, leading to an enhancement of the exchange, i.e. the Curie temperature, and to a decrease of the moment. An extra polarization, as previously found from the study of magnetization density maps, is confirmed and discussed.

1. Introduction

The CeRh_3B_2 intermetallic compound exhibits quite peculiar magnetic properties. It is ferromagnetic, with an exceptionally high Curie temperature $T_C \approx 115$ K [1]. This temperature is by far the highest magnetic ordering temperature ever found in a compound in which cerium is alloyed with non-magnetic elements. It is even higher than that (105 K [2]) of the isostructural GdRh_3B_2 compound, in total disagreement with the classical de Gennes scaling. Despite this huge value of T_C , CeRh_3B_2 exhibits an abnormally small spontaneous magnetization. Magnetic measurements on single crystals show a strong anisotropy. The

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easy magnetization [3] is within the c -plane of the hexagonal structure, with a measured magnetization at low temperature of only $\approx 0.4 \mu_B/\text{fu}$. This value is strongly reduced compared to the saturated Ce^{3+} value ($2.14 \mu_B$). A more recent paper [4] points out an anisotropy of the saturation magnetization within the basal plane, with a measured difference of $0.004 \mu_B/\text{fu}$ between the a and a^* directions. In the paramagnetic range, the magnetic susceptibility does not follow a Curie–Weiss law until 600 K.

The CeRh_3B_2 crystal structure is hexagonal, of CeCo_3B_2 -type, with the Ce site located at the origin of the cell (point symmetry $6/mmm$). A peculiar feature of the RRh_3B_2 crystal structure is a much smaller c lattice parameter than the a one: in the cerium compound at room temperature $c = 3.09 \text{ \AA}$ and $a = 5.48 \text{ \AA}$. It turns out that the Ce atoms form chains along the c direction, with very short Ce–Ce distances, even smaller than in α -Ce (3.41 \AA). Moreover, Langen *et al* [5] have reported a quite abnormal thermal variation of the lattice parameters. When cooling down from 1100 K to 4 K, a and c first decrease similarly as in the neighboring compounds PrRh_3B_2 and LaRh_3B_2 . Around 800 K, the slope of a becomes weaker and a shallow minimum is observed before a drastic increase between 300 and 100 K. On the contrary, below 800 K, c decreases more quickly than in PrRh_3B_2 or LaRh_3B_2 and is strongly reduced below 300 K. These variations correspond to a flattening of the cell, intensifying the difference between the c and a lattice parameters. In the whole temperature range, c remains smaller than in PrRh_3B_2 . Such small Ce–Ce distances can lead to strong hybridization between the Ce-4f, Ce-5d and conduction electrons and to strong crystal electric field (CEF) effects [6, 7].

A CEF peak has in fact been observed around 170 meV by inelastic neutron scattering [8]. Contributions of the excited multiplet $J' = 7/2$ lying at around 280 meV [9] from the Ce ground multiplet $J = 5/2$ are no longer negligible and have to be present in the wavefunctions of all energy levels, even the fundamental one. So, all the calculations including the Ce wavefunctions have to take into account this excited multiplet. This has already been done successfully for the Ce magnetic form factor [10], determined from polarized neutron diffraction [11], allowing a determination of possible sets of exchange and CEF parameters. These two multiplet calculations have given a much better agreement of the magnetic form factor than calculations with only the ground state multiplet. The magnetic density maps obtained from these experiments performed in fields applied along an easy direction lead to the following magnetization distribution: no magnetization on the Rh and B sites, a 4f-type moment on the Ce site and a large opposite diffuse contribution of 5d-type, very anisotropic and lying between the Ce atoms along the c chains only. This conduction electron polarization was found to be proportional to the spin part of the 4f moment and was not observed at 150 K.

The aim of this paper is to show that these two multiplet calculations can also well account for the observed values of magnetizations and susceptibilities along the easy and hard directions. Spin and orbital parts of the Ce-4f moment are calculated and discussed.

2. Experimental details and results

2.1. Experimental details

In order to gather magnetic information on a single sample, the studied CeRh_3B_2 crystal was the same as that already measured by polarized neutron diffraction in [10, 11]. Its shape is a platelet of $2.0 \times 1.5 \times 3.6 \text{ mm}^3$, the long dimension being along the c direction. A crystal four times bigger was also used to confirm the measurements at high temperature when the signal becomes very weak.

Magnetization measurements were performed between 4 K and room temperature using an extraction method. The first measurements were done in a Quantum Design SQUID

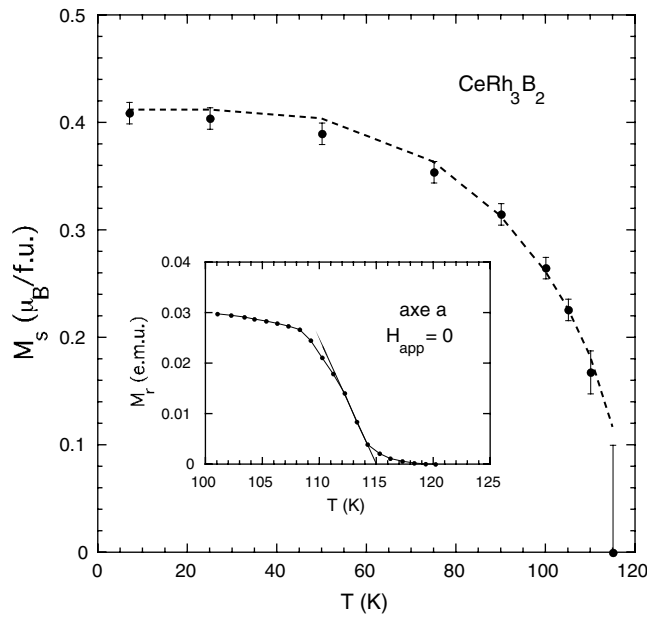


Figure 1. Thermal variation of the spontaneous magnetization. The dotted line is calculated with the parameters $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0\langle r^2 \rangle = -7500$ K, $A_4^0\langle r^4 \rangle = 633$ K, $A_6^0\langle r^6 \rangle = -350$ K, $A_6^6\langle r^6 \rangle = 0$ and $(K_{\text{pol}})_a = 0.12$ (see text). Inset: thermal variation of the remanent magnetization M_r near T_C . The lines are guides for the eye.

magnetometer at the DRFMC (CEA-Grenoble) in fields up to 5 T. The sensitivity of the measurements was $\approx 10^{-9}$ A m² ($= 10^{-6}$ emu). In order to minimize extra contributions, the sample was wedged inside a straw. Measurements along the easy magnetization direction were also performed with the sample just hung by a thread. The contribution of the straw could then be evaluated for corrections along the hard direction.

Other magnetization curves were obtained in a superconducting coil at the Institut Néel (CNRS-Grenoble) in fields up to 10 T, with a sensitivity of $\approx 10^{-6}$ A m². The sample was oriented along the desired crystallographic directions and glued into a sample holder, especially to avoid a rotation when fields were applied along directions other than the easy one. The empty sample holder was also measured in the same conditions for appropriate corrections.

Despite the high absolute sensitivity of these devices, one should keep in mind that the actual accuracy of the magnetic measurements is limited by other sources of error, such as disorientation of the crystal, sample holder corrections, centering of the sample, etc.

2.2. Results

The magnetization versus applied field curves confirm the ferromagnetic behavior of the CeRh₃B₂ compound, with the easy magnetization in the basal plane of the hexagonal structure whereas the c direction is a hard magnetization axis. The value of the Curie temperature of our sample $T_C = 115(\pm 1)$ K was obtained from the thermal variation of the remanent magnetization M_r (in zero applied field) along the a direction (inset of figure 1).

The magnetization curves along the a direction show a spontaneous magnetization M_s at temperatures below 115 K. The M_s values were precisely determined from the Arrott plots [12], $M^2 = f(H/M)$, where $H = H_{\text{app}} - H_d$ is the field corrected from the demagnetizing field H_d .

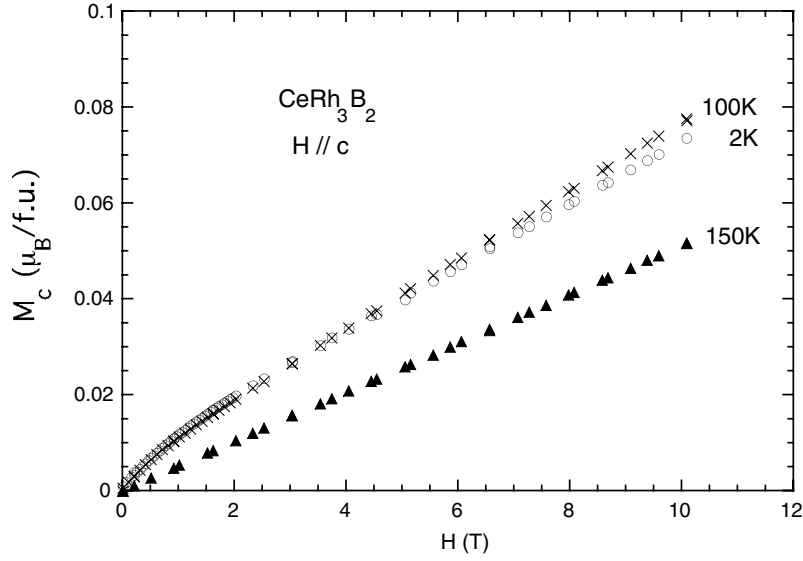


Figure 2. Magnetization curves for field applied along the c direction at $T = 2, 100$ and 150 K.

These plots present a linear behavior and at each temperature the intercept with the M^2 -axis gives M_s^2 . The obtained M_s thermal variation is reported in figure 1. Along the a direction M_s reaches $0.41(\pm 0.01) \mu_B/\text{f.u.}$ at 2 K and magnetization curves along other directions in the basal plane lead to the same value.

For fields applied along the c direction, the $M(H)$ curves of the measurements in the SQUID, with the sample inside a straw, presented a small spontaneous magnetization ($\approx 0.04 \mu_B/\text{f.u.}$), one order of magnitude lower than that along the easy direction. This ‘pseudo’ spontaneous magnetization disappeared at T_C . The same behavior was also observed by Galatanu *et al* [4] in their figure 1. As such a result is in contradiction with a collinear ferromagnetic structure, we undertook new measurements in which the sample was oriented along c and glued on a sample holder. The data corrected for the sample holder contribution are shown in figure 2: although a very small curvature remains below 1 T, the magnetization increases regularly and linearly with the applied field and there is no spontaneous contribution. As temperature is increased up to T_C , the magnetization measured along c increases. Indeed as the anisotropy progressively reduces when increasing the temperature, the magnetization rotates more easily from the easy axis towards the applied field. The presence of the ‘pseudo’ spontaneous magnetization along c as observed in our first measurements using a SQUID magnetometer and as published by Galatanu *et al* [4] can be well accounted for by a disorientation of the crystal of $\approx 8^\circ$. In our case, this disorientation could be due, because of the very strong anisotropy, to a rotation of the crystal (or of the straw) under the effect of the magnetic field applied along the hard axis.

Figure 3 gathers the magnetization curves along the easy and hard directions at the same temperature $T = 2$ K.

Above T_C , the magnetizations measured along a and c vary linearly with the applied field. In order to increase the magnetic signal, curves for the field applied along the c hard axis above $T = 200$ K were obtained on the biggest crystal glued on the sample holder. At lower temperatures, results on both crystals were identical. The inverse magnetic susceptibilities were also determined from the Arrott plots [12] (intercept of the M^2 straight lines with the

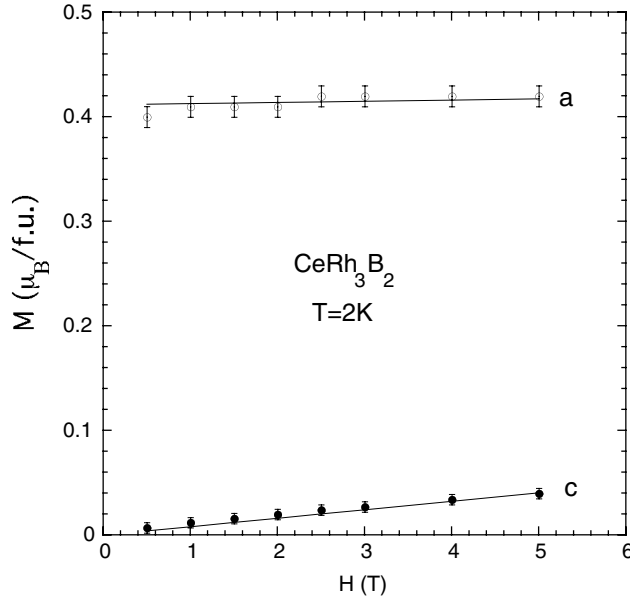


Figure 3. Magnetization curves along the easy and hard directions at $T = 2$ K. Full lines are calculated with the parameters $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K, $A_6^0(r^6) = -350$ Kc, $A_6^6(r^6) = 0$, $(K_{\text{pol}})_a = 0.12$ and $(K_{\text{pol}})_c = 0.40$ (see text).

H/M -axis). Their thermal variations are drawn in figure 4 for the a and c directions. As already noticed in [4], a Curie–Weiss variation is not observed in our studied temperature range (below room temperature) and a strong anisotropy is still present in the paramagnetic state.

3. Crystal electric field analysis

3.1. Model

The measured CeRh_3B_2 bulk magnetization M results from two contributions: (i) a Ce 4f-type moment μ_{4f} depending on the wavefunctions of the populated electronic levels and (ii) a diffuse magnetization μ_{pol} associated with the conduction-electron polarization. Energy states and their wavefunctions are obtained from diagonalizing the Hamiltonian of the system. We have already performed such calculations, taking into account both multiplets of cerium $J = 5/2$ and $J' = 7/2$, to explain the anisotropy observed in the Ce-4f magnetic form factor [10], and the complete formalism is explained in that article. The polarization was found to be proportional to the spin part μ_{4f}^S of the 4f moment μ_{4f} , as in several samarium compounds [13].

The Hamiltonian is composed of five contributions: spin–orbit coupling, crystalline electric field (CEF), exchange interaction, Zeeman effect and polarization of conduction electrons. It can be written as:

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S} + \mathcal{H}_{\text{CF}} - 2J_{\text{ff}} \langle S \rangle \mathbf{S} + \mu_{\text{B}} \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}) + 2\mu_{\text{B}} K_{\text{pol}} \mathbf{H} \cdot \mathbf{S}$$

where \mathbf{L} and \mathbf{S} are respectively the orbital and spin operators, μ_{B} is the Bohr magneton and \mathbf{H} the external field. For cerium, the value of the spin–orbit coupling coefficient λ was taken as 930 K ($\lambda = \Delta/J'$ with $\Delta = 280$ meV or 3250 K [9]). The exchange is considered in the mean field approximation to be proportional to \mathbf{S} through the exchange interaction J_{ff} . The conduction electron polarization term is also proportional to \mathbf{S} with a polarization parameter K_{pol} . For calculating the magnetic form factor, the polarization term was not introduced

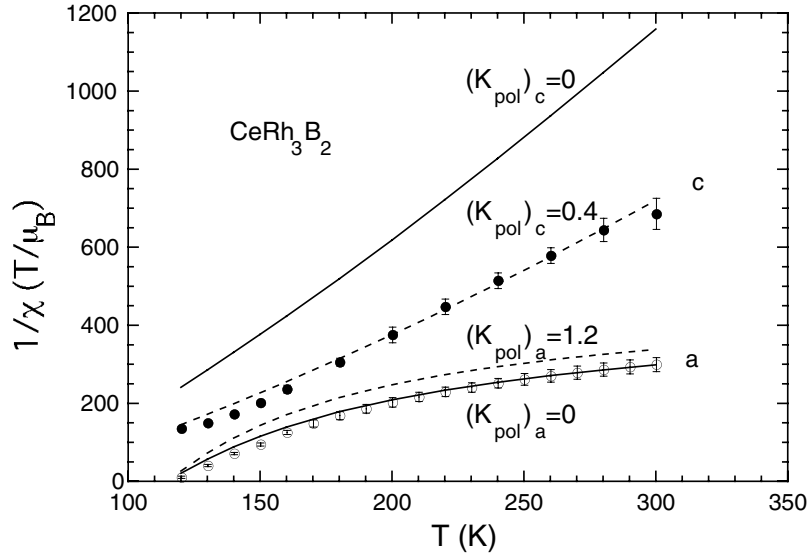


Figure 4. Thermal variation of the inverse magnetic susceptibility along *a* and *c* directions. Lines are calculated with the parameters $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K and $A_6^0(r^6) = 0$. $A_6^0(r^6)$ is extrapolated from values at 150 and 300 K. $(K_{\text{pol}})_a$ and $(K_{\text{pol}})_c$ are either equal to the low temperature values (dotted lines) or equal to zero (full lines).

because only data above $\sin \theta/\lambda \approx 0.2 \text{ \AA}^{-1}$ were used for the refinements. The form factor of a delocalized magnetization has vanished above this value.

The CEF Hamiltonian for systems including several multiplets can be calculated [14] by the tensor operator techniques of Racah [15] and is then expressed in a way similar to the Stevens formalism:

$$\mathcal{H}_{\text{CF}} = \sum_{k,q} N_k^q A_k^q(r^k) U_k^q$$

the N_k^q and U_k^q terms are tabulated [16, 10]. The $A_k^q(r^k)$ are the CEF parameters. For hexagonal symmetry, there are four independent ones: $A_2^0(r^2)$, $A_4^0(r^4)$, $A_6^0(r^6)$ and $A_6^6(r^6)$ (called $(B_k^q)_c$ in our previous paper [10]). In fact, they correspond to the B_k^q/θ_n of Hutchings with θ_n being the Stevens coefficients α , β and γ used for one-multiplet calculations [17, 18]. For the Ce^{3+} ion, the value of γ is zero and the 6th order terms $A_6^0(r^6)$ and $A_6^6(r^6)$ do not play any role in calculations within the fundamental multiplet.

One possible set of parameters proposed to fit the Ce-4f magnetic form factor in CeRh_3B_2 , with respect to the observed CEF splitting, was: $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 650$ K, $A_6^0(r^6) = -350$ K and $A_6^6(r^6) = 0$ [10]. The value of the exchange interaction was mainly determined by the fit of the Curie temperature. Concerning the four CEF parameters, they are strongly correlated. $A_6^6(r^6)$ was found to have no influence on the calculated form factors and was fixed to zero. $A_2^0(r^2)$ has to be negative for an easy magnetization lying in the basal plane, and to any value of $A_2^0(r^2)$ down to $-10\,000$ K there is a corresponding set of parameters $A_4^0(r^4)$ and $A_6^0(r^6)$ leading to the same splitting and to the same wavefunction of the ground state. The proposed set of CEF parameters is thus not unique.

No satisfying fitting could be obtained without introducing a reduction factor of the 4f moment. As a matter of fact, all the wavefunctions which are compatible with the observed anisotropy of the magnetic form factor [10] and with moments lying in the basal plane

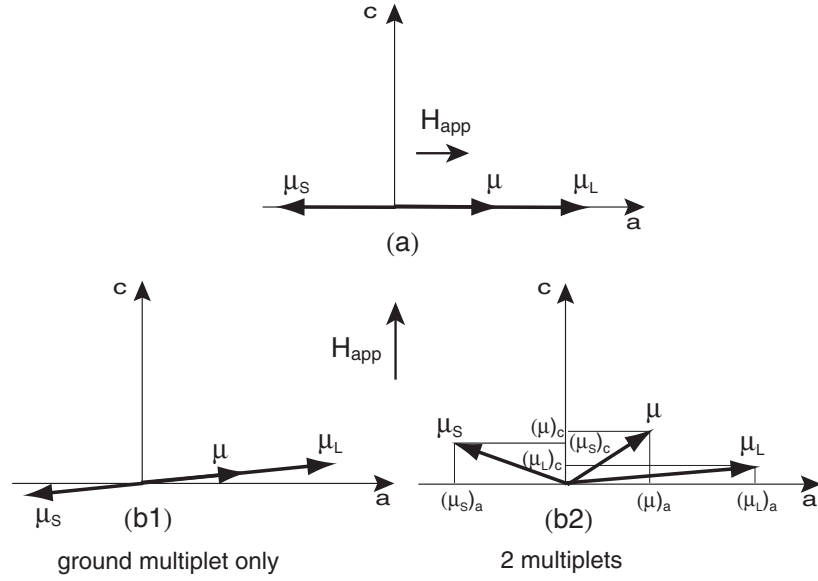


Figure 5. Directions of the orbital μ^L , spin μ^S and total μ 4f moments, for fields applied: (a) along the easy a direction, (b) along the hard c direction: (b1) in case of ground multiplet only, (b2) in case of two multiplets. The rotation of the moments are amplified for a better understanding.

($A_2^0\langle r^2 \rangle$ negative) lead to too large values of this moment and a scaling factor $K_0 = 0.67$ had to be introduced. It is a phenomenological way to consider the effects of a strong hybridization which reduces the localized Ce-4f moment [19]. Such reduction factors have already been used in other cerium compounds, the largest effect (≈ 0.5) being found in the Kondo compound CeAl₂ [20].

3.2. Ferromagnetic state

In the ferromagnetic state, a more precise determination of the various parameters has been obtained by a simultaneous refinement on different kinds of data: Ce-4f magnetic form factor, position of the first excited doublet [8], dependences on the applied field or temperature of the magnetization along the easy a and hard c directions. For the fixed values of $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0\langle r^2 \rangle = -7500$ K and $A_6^0\langle r^6 \rangle = 0$, we find:

$$A_4^0\langle r^4 \rangle = 633(6) \text{ K}, \quad A_6^0\langle r^6 \rangle = -350(4) \text{ K} \quad \text{and} \quad (K_{\text{pol}})_a = 0.12. \quad (1)$$

As the spin part $(\mu_{4f}^S)_a$ is negative, the polarization contribution $(\mu_{\text{pol}})_a = (K_{\text{pol}})_a \cdot (\mu_{4f}^S)_a$ is opposite to the moment along a (figure 5(a) and table 1). The thermal variation of M_s (in zero applied field) and the magnetization curve at 2 K in a field applied along a have been calculated with these parameters and are drawn in figures 1 and 3, respectively.

When the field is applied along c , the orbital and spin parts of the 4f moment are no longer strictly linked as when considering the ground multiplet only (see figure 5(b1)) but are reoriented along the field direction (see figure 5(b2)). In fact, the anisotropy is so large that the resulting moment $(\mu_{4f})_c$ along c is very small, whereas a large component $(\mu_{4f})_a$ remains along a . The corresponding angle of rotation, at $T = 2$ K and in $H = 10$ T, deduced from the ratio of the two components $(\mu_{4f})_c/(\mu_{4f})_a$ is 5.0° for the spin part μ_{4f}^S and 0.9° for the orbital part μ_{4f}^L .

Table 1. Calculation at $T = 2$ K of the polarization μ_{pol} along the direction of the applied field H for various values of the polarization coefficient (K_{pol}) and comparison of the resulting calculated moment M with the experimental one M_{exp} . Parameters for the moments calculation are $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K, $A_6^0(r^6) = -350$ K and $A_6^6(r^6) = 0$.

T (K)	$H \parallel a$ (T)	$(\mu_{4f})_a$ (μ_B/fu)	$(\mu_{4f}^S)_a$ (μ_B/fu)	$(K_{\text{pol}})_a$	$(\mu_{\text{pol}})_a$ (μ_B/fu)	M_a (μ_B/fu)	$(M_{\text{exp}})_a$ (μ_B/fu)
2	5	0.482	-0.537	0.12(1)	-0.064(5)	0.418(5)	0.42(1)
T (K)	$H \parallel c$ (T)	$(\mu_{4f})_c$ (μ_B/fu)	$(\mu_{4f}^S)_c$ (μ_B/fu)	$(K_{\text{pol}})_c$	$(\mu_{\text{pol}})_c$ (μ_B/fu)	M_c (μ_B/fu)	$(M_{\text{exp}})_c$ (μ_B/fu)
2	10	0.062	0.046	0.12(1)	0.006(1)	0.068(1)	0.075(5)
2	10	0.062	0.046	0.40(5)	0.018(3)	0.080(3)	0.075(5)

Table 2. Energies of the first excited doublet at various temperatures: observed E_{obs} and calculated E_{calc} with $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K, $A_6^0(r^6) = 0$ and various values of $A_6^6(r^6)$. (ΔE) are their variations relative to the value at $T = 2$ K.

T (K)	E_{obs} (meV)	$(\Delta E)_{\text{obs}}$ (meV)	$A_6^6(r^6)$ (K)	E_{calc} (meV)	$(\Delta E)_{\text{calc}}$ (meV)
2	167.0(0.6)		-350	166.4	
150	150.0(1.4)	17.0(2.0)	-350	156.6	9.8
150	150.0(1.4)	17.0(2.0)	-311	148.6	17.8
300	132.0(2.6)	35.0(3.2)	-218	130.6	35.8

The polarization $(\mu_{\text{pol}})_c = (K_{\text{pol}})_c \cdot (\mu_{4f}^S)_c$ is then parallel to the field and adds itself to the moment $(\mu_{4f})_c$. Table 1 shows that if the polarization parameter is isotropic ($(K_{\text{pol}})_c = (K_{\text{pol}})_a = 0.12$), the total magnetization calculated along c is too small. A much larger value of this coefficient has to be used: $(K_{\text{pol}})_c = 0.40 \pm 0.05$. Such a conclusion can be related to the very short distance between Ce atoms in that direction. The calculated magnetization curve along c at 2 K is shown in figure 3.

The good agreement between all calculated and experimental data in the whole temperature range below T_C confirms the validity of the chosen parameters in the ferromagnetic state.

3.3. Paramagnetic state

Inelastic neutron spectroscopy (INS) measurements were also performed at two temperatures in the paramagnetic state (150 and 300 K), besides those in the ferromagnetic state (18 K) [8]. They present a shift towards lower energies of the position of the CEF peak characteristic of the transition to the first excited doublet, given by the energy E_{obs} (table 2). The change between $T = 18$ K and $T = 150$ K can be partially attributed to the fact that the exchange field is no longer active. However, the corresponding calculated variation is 10 meV while the observed change is about 17 meV. Between $T = 150$ K and $T = 300$ K, the energy of the doublet is again decreased by 18 meV, which can be explained only by a change in the CEF parameters. These changes must be related to the quite abnormal thermal dependence of the lattice parameters, especially between 100 and 300 K [5].

The CEF parameters at 150 and 300 K have been calculated by assuming that $A_4^0(r^4)$ remains constant while $A_6^0(r^6)$ could vary. The fits on the positions of the INS peaks at 150 and 300 K, together with the magnetic form factor for $T = 150$ K, lead to new values of

Table 3. Contributions from the different multiplets to the orbital, spin and total 4f moments of the ground state (μ_{4f}^L , μ_{4f}^S and μ_{4f} , respectively) calculated in a zero applied field with the parameters $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K, $A_6^0(r^6) = -350$ K and $A_6^6(r^6) = 0$.

Multiplet contribution	μ_{4f}^L (μ_B/fu)	μ_{4f}^S (μ_B/fu)	μ_{4f} (μ_B/fu)
5/2-5/2	1.039	-0.260	0.779
7/2-7/2	-0.140	-0.047	-0.187
7/2-5/2	0.115	-0.230	-0.115
Total	1.014	-0.537	0.477

$A_6^0(r^6)$ given in table 2, which are decreasing as temperature increases. The lattice parameters of CeRh_3B_2 show a more normal behavior at high temperatures, and it therefore seems justified that the sixth-order term contribution vanishes, approaching the zero contribution as in classical Ce compounds.

The values of $A_6^0(r^6)$ at other temperatures in the paramagnetic range were then deduced from those at 150 and 300 K by a linear extrapolation. They were used for calculating the reciprocal susceptibilities along the *a* and *c* directions with assumed values for K_{pol} either identical to those in the ferromagnetic state ($(K_{\text{pol}})_a = 0.12$ and $(K_{\text{pol}})_c = 0.40$) or zero. Calculated curves are compared to the experimental data in figure 4. For $(1/\chi)_a$, the assumption of an absence of polarization above T_C ($(K_{\text{pol}})_a = 0$) fits the measurements very well. On the contrary, this assumption is in complete disagreement for $(1/\chi)_c$. Calculations with $(K_{\text{pol}})_c = 0.40$ (same as in the ferromagnetic state) are in much better agreement with the experimental results.

4. Discussion

All these magnetization measurements can be well accounted for by our model introducing the role of the spin-orbit coupling. The contribution of the excited $J' = 7/2$ multiplet is essential, as already noticed when calculating the Ce magnetic form factor [10]. In the ferromagnetic state, the ground-state wavefunction in zero field calculated with the set of parameters $K_0 = 0.67$, $J_{\text{ff}} = 570$ K, $A_2^0(r^2) = -7500$ K, $A_4^0(r^4) = 633$ K, $A_6^0(r^6) = -350$ K and $A_6^6(r^6) = 0$, can be written as:

$$|\psi_0\rangle = 0.314|5/2, 3/2\rangle + 0.458|5/2, \bar{1}/2\rangle + 0.748|5/2, \bar{5}/2\rangle \\ + 0.261|7/2, 7/2\rangle + 0.177|7/2, 3/2\rangle + 0.142|7/2, \bar{1}/2\rangle + 0.110|7/2, \bar{5}/2\rangle.$$

The terms from the $J = 5/2$ multiplet are still preponderant but the contribution of the terms from the $J' = 7/2$ multiplet is far from negligible. One main consequence is an increase in the spin part μ_{4f}^S of the 4f moment: it is almost doubled (from -0.26 to $-0.54 \mu_B/\text{fu}$), as can be seen in table 3 where the different contributions to the spin and orbital moments are reported. As the spin part is opposite to the orbital part, which is much less influenced by the $J' = 7/2$ contribution, the resulting moment μ_{4f} is strongly reduced from 0.78 to $0.48 \mu_B/\text{fu}$. Moreover, the exchange interaction, which is related to the value of the spin, is also raised. Thus, taking into account the excited multiplet leads to a higher ordering temperature together with a lower value of the moment.

Extra parameters have to be considered to fit the measured magnetizations properly. As shown by the magnetization density maps obtained under a magnetic field applied along an

easy magnetization direction [10], a negative diffuse density, associated with a polarization of conduction electrons, is present along the c chains in the ferromagnetic phase and disappears in the paramagnetic phase. By fitting the magnetization and inverse susceptibility curves along a , we have confirmed the presence of a polarization contribution $(\mu_{\text{pol}})_a$ proportional to the spin moment, which vanishes in the paramagnetic domain. A polarization $(\mu_{\text{pol}})_c$ has also been found for fields applied along the hard c direction, the polarization coefficient $(K_{\text{pol}})_c$ being much larger in that direction (0.40 compared to 0.12) and constant in the whole temperature range. Note that although the polarization coefficients along the two a and c directions are both positive, the resulting polarization is either opposite to the 4f moment if H is along a or in the same direction if H is along c . From the polarized neutron results [10], we can assert that this polarization correction on the 4f magnetization is totally independent of the reduction coefficient K_0 . In fact, the magnetic form factor is sensitive to K_0 at all diffraction angles whereas the diffuse polarization is seen only at low values of $\sin\theta/\lambda$.

Another consequence of the influence of the $J' = 7/2$ multiplet is the role of sixth-order terms in the CEF Hamiltonian, terms which are inoperative if only the ground state multiplet is considered. The $A_6^0\langle r^6 \rangle$ term is necessary to get anisotropy inside the basal plane and the very weak differences in magnetizations in that plane observed by Galatanu *et al* [4] cannot exist within only one multiplet formalism. In our two multiplet calculations, we have supposed that $A_6^0\langle r^6 \rangle = 0$ and we therefore find no anisotropy inside the easy c plane. Furthermore, even for very large values of $A_6^0\langle r^6 \rangle$, the calculated anisotropy is insignificant. In fact, despite the high sensitivity of the measuring device, many features can perturb the measurements, especially a small disorientation of the crystal or non-identical centerings of the sample. As their measurements along the c direction were characteristic of a disorientation of the crystal, we do not have much confidence in their result concerning an anisotropy in the basal plane.

The bulk magnetization and the magnetic Ce form factor are determined only by the wavefunctions of the ground doublet. As already mentioned, several sets of CEF parameters lead to the same wavefunctions. This study enables us to reach this ground state wavefunction but not the absolute values of the three main CEF parameters. However, they are correlated, and the value chosen for $A_2^0\langle r^2 \rangle$ involves the values of $A_4^0\langle r^4 \rangle$ and $A_6^0\langle r^6 \rangle$. Whatever the chosen CEF parameters, the CEF splitting is extremely large and the difference between the two first doublets is more than 1500 K. In the studied temperature range, only the ground doublet is then occupied (99.4% at 300 K) and its associated moment in the paramagnetic state calculated with our CEF parameters is anisotropic like the reverse susceptibilities. The values at 300 K are $\pm 0.95 \mu_B/\text{fu}$ in the basal plane and $\pm 0.67 \mu_B/\text{fu}$ along the c -axis.

5. Conclusion

In conclusion, our magnetization measurements confirm the important role of the second multiplet of the Ce^{3+} ion on the magnetic properties of the CeRh_3B_2 compound. The apparently conflicting high Curie temperature and small magnetic moment are partially explained. A reduction factor of the 4f moment and an extra magnetic polarization proportional to its spin part, as previously indicated by the polarized neutron diffraction results, are confirmed by the entire magnetization variations.

All these quite peculiar properties are to be related to the crystal structure of CeRh_3B_2 , with very short distances between Ce atoms along the c direction, shorter than in all other cerium compounds. These features lead to very high crystalline electric field effects with strongly anisotropic properties and to large hybridization between 4f and conduction electrons.

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